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Treatment of Ammonia Plant Process Condensate Effluent

Louisiana Chemical Association, Baton Rouge

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TREATMENT OF AMMONIA PLANT PROCESS CONDENSATE EFFLUENT

by

C.J. Romero, F. Yocum,
J.H. Mayes and D.A. Brown
(Gulf South Research Institute)

Louisiana Chemical Association
231 Florida Street
300 Taylor Building
Baton Rouge, Louisiana 70801

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Industrial Environmental Research Laboratory
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SECTION 1

INTRODUCTION

Compounds containing the element nitrogen are becoming increasingly important in wastewater management programs because of the many effects that nitrogenous materials in wastewater effluent can have on the environment. In its various forms, nitrogen can deplete dissolved oxygen levels in receiving waters, stimulate aquatic growth, exhibit toxicity toward aquatic life, affect chlorine disinfection efficiency, present a public health hazard, and affect the suitability of wastewater for reuse. Biological and chemical processes which occur in wastewater treatment plants and in the natural environment can change the chemical form in which nitrogen exists. Such changes may eliminate one deleterious effect of nitrogen while producing, or leaving unchanged, another effect. It is important, therefore, to review the chemistry of nitrogen and the effects that the various resulting compounds can have on the environment prior to the detailed discussion of the results of this grant program.

The relationship among the various nitrogen compounds and the transformations which can occur may be presented schematically in a diagram known as the nitrogen cycle, which is illustrated in Figure 1. The atmosphere serves as the ultimate reservoir of nitrogen gas. From this reservoir, nitrogen is removed naturally by electrical discharge and artificially by chemical manufacturing. The nitrogen gas is returned to the atmosphere by the action of denitrifying organisms. In the fixed state, nitrogen can undergo the various reactions shown in the nitrogen cycle diagram. The aspects of particular importance to the grant program and its effect on surface waters are discussed in detail later in this report.

THE NITROGEN CYCLE RELATED TO SURFACE WATER

Since the presence of nitrogen is essential to aquatic and marine life in certain regulated amounts, there is a balanced cycle of its presence within surface waters. Nitrogen may be added to this system any of several ways:

Natural Sources

1. Atmospheric nitrogen fixation solution and dispersion by rain.
2. Atmospheric nitrogen fixation and dispersion through contact and subsequent fallout.
3. Atmospheric nitrogen fixation by algae and bacterial species.
4. Presence in subsurface ground water, surface entrance and subsequent runoff.

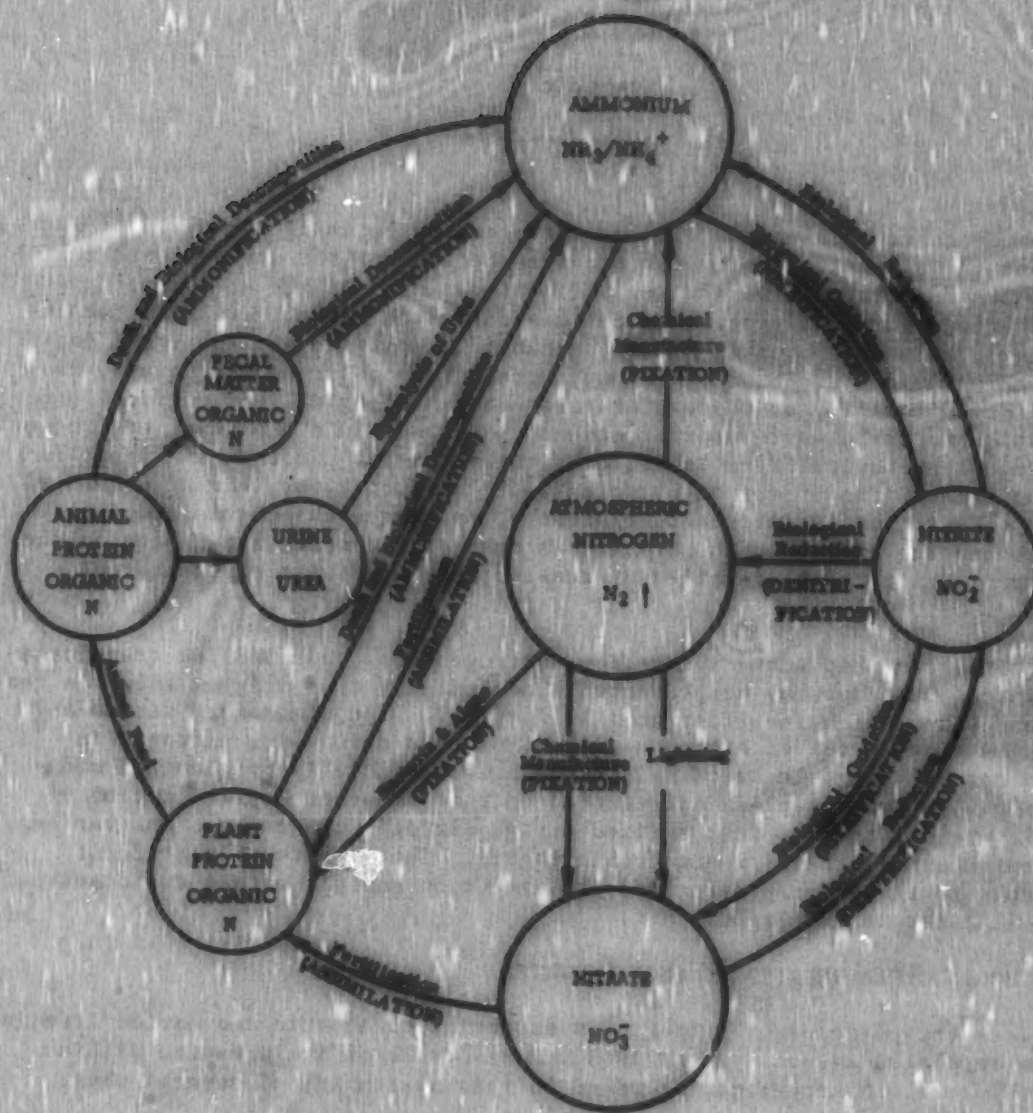


Figure 1. The nitrogen cycle.

Man-Caused Sources

1. Industrial wastewaters contaminated with various compounds of nitrogen.
2. Agricultural runoff from land containing previously applied nitrogenous fertilizers.

Natural Sources

Ammonification, nitrification, assimilation, and denitrification can occur within the aquatic environment. Ammonifications of organic matter are carried out by microorganisms. The ammonium thus formed can be assimilated by algae and aquatic plants, and the resultant growths can create water quality problems.

Nitrification of ammonium can occur with a resulting depletion of the dissolved oxygen content of the water. To oxidize 1.0 mg/l of ammonia-nitrogen, 4.6 mg/l oxygen is required. Denitrification produces nitrogen gas which may escape to the atmosphere. Because anoxic conditions are required, the oxygen-deficient hypolimnion (or lower layer) of lakes and the sediment layer of streams and lakes are important zones of denitrification action.

Man-Caused Sources of Nitrogen in Waters

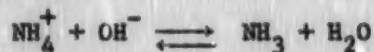
The activities of man have increased naturally-occurring quantities of nitrogenous compounds in the aquatic environment. These sources have been principally (1) fertilization of agricultural land, (2) combustion of fossil fuels, (3) wastewater from fertilizer manufacturing facilities, (4) wastewaters from other organic-based production facilities, and (5) other sources such as livestock feed lots, poultry and egg production. These manmade sources can affect the environment through biostimulation of surface water, toxic contributions to surface waters, and contamination of drinking water.

Biostimulation of Surface Waters--

A major problem in the field of water pollution is eutrophication, excessive plant growth and/or algae "blooms" resulting from over-fertilization of rivers, lakes, and estuaries. Results of eutrophication include deterioration in the appearance of waters, odor problems from decomposing algae, and lower dissolved oxygen levels which can adversely affect fish life. Eutrophication is of most concern in lakes because nutrients which enter tend to be recycled within the lake and build up over a period of time.

Toxic Contributions to Surface Waters--

The principal toxicity problem is from ammonia in the molecular form (NH_3) which can adversely affect fish life in receiving waters. A slight increase in pH may cause a great increase in toxicity as the ammonium ion (NH_4^+) is transformed to ammonia in accordance with the following equation.

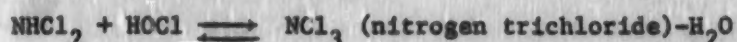
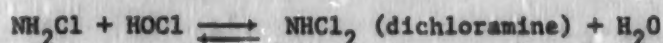
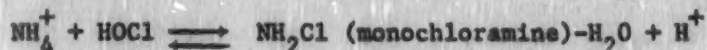


Factors which may increase ammonia toxicity at a given pH are: greater concentrations of dissolved oxygen and carbon dioxide; elevated temperatures;

and bicarbonate alkalinity. Reported levels at which acute toxicity is detectable have ranged from 0.01 mg/l to over 2.0 mg/l of molecular ammonia-nitrogen.

Public Health Considerations--

When chlorine, in the form of chlorine gas or hypochlorite salt, is added to wastewater containing ammonium, chloramines, which are less effective disinfectants, are formed. The major reactions are as follows:



Only after the addition of large quantities of chlorine does free available chlorine exist. If the effluent ammonia-nitrogen concentration were 20 mg/l, about 200 mg/l of chlorine would be required to complete the reactions with ammonium and organic compounds. Only rarely is this level of chlorine addition ("breakpoint" chlorination) used in wastewater treatment. Obviously, ammonia would have to be present in large quantities in any industrial effluent to cause any serious disinfectant problem through chlorine losses.

SECTION 2

SUMMARY AND CONCLUSIONS

Based on a survey of the fertilizer industry, the guidelines division of the Environmental Protection Agency promulgated discharge standards for ammonia producers on April 8, 1974. These effluent limitation guidelines set the amount of ammonia which could be discharged from a plant process condensate as 50 kg/day. This represented an average 50 mg/l concentration in the process effluent from a 907 m. ton/day ammonia plant discharging an average 757 l/min from the process area.

Recognizing that the problem of meeting this limitation existed in plants whose only product was ammonia, Louisiana ammonia producers sought to develop the necessary technology to meet the guidelines. Since the only product for the majority of the ammonia producers in Louisiana is anhydrous ammonia, a wide base for program development was established. Through their industrial membership in the Louisiana Chemical Association (LCA), a joint research grant involving the EPA and LCA was established. The participants were as follows:

1. Louisiana State Science Foundation
2. Environmental Protection Agency Industrial and Environmental Research Laboratory
3. Participating companies through the Louisiana Chemical Association
 - a. Air Products and Chemicals, Inc.
 - b. American Cyanamide Company
 - c. Borden Chemical Company
 - d. C.F. Industries, Inc.
 - e. W.R. Grace & Company
 - f. I.M.C. Corporation
 - g. Monsanto Company
 - h. Olin Corporation

CHARACTERIZATIONS OF AMMONIA PLANT PROCESS CONDENSATE

Contaminant Identification

Seven different plant process condensate sources were represented by the production operations of the eight participating industries. Each representative stream was analyzed for the ammonia, methanol, and carbon dioxide components. The analytical results of all samples for each stream were averaged and are presented in Table 1. For each process involved, the catalyst age and sever-

TABLE 1. METHANOL, AMMONIA, AND CARBON DIOXIDE CONCENTRATIONS

Stream Number	Ammonia (mg/l)	Methanol (mg/l)	Carbon Dioxide (mg/l)
100	800	459	1,137
200	1,041	362	2,470
300	858	618	2,559
400	1,015	972	2,789
500	825	559	1,258
600	700	172	642
Average	873	524	1,809

ity of operation (amount of condensate or excess steam) was noted.

Metal analysis was performed on samples for each stream to determine copper, nickel, iron, zinc and chromium concentrations. Such metal contaminants could affect the process for one of the proposed treatment methods calling for reinjection of the stripper overhead in the reformer feed stream. Samples were obtained in propylene containers for laboratory purposes. Analyses of the samples indicated that no trace metal contaminant problem existed if reinjection of the stripped condensate back into the process was contemplated. Metal analyses results are reported in Table 2.

BENCH-SCALE DATA

A review of stream characterization data indicated that stream 700 was too low in ammonia, methanol, and carbon dioxide concentration to be classified as a representative sample stream. Therefore, values for stream 700 are deleted. Table 1 shows concentrations of the three contaminants from representative streams, the average values being ammonia, 873 mg/l; methanol, 524 mg/l; and carbon dioxide, 1809 mg/l. Four representative streams were selected for bench-scale steam stripping tests; 100, 200, 300 and 400. A total of 61 runs was made utilizing the process condensates from these four production sources.

Process Effluent from Company 100

Initially the pilot steam stripper contained a packed bed depth of 2.2 m using 6 mm (1/4 inch) Rasching rings. Results of runs 1-7 indicated that steam stripping the process condensate was feasible but did not produce desired ammonia and methanol concentrations in the effluent bottoms. Bottoms from runs 5, 6, and 7 of pilot steam stripper were collected and stored to determine if additional packing height would be required. These collected bottoms were reprocessed through the pilot steam stripper as feed (for runs 8, 9, and 10) to determine if further separation of ammonia, methanol and carbon dioxide would take place. Similarly, run 10 overheads were collected and used as feed for run 11. Results indicated that additional packing height would reduce the ammonia, methanol, and carbon dioxide concentration for a single once-through run in the pilot steam stripper.

TABLE 2. METAL ANALYSES

Sample I.D.	Cu mg/l	Ni mg/l	Fe mg/l	Zn mg/l	Cr mg/l
<u>Company No. 100</u>					
Feed	<0.5	<0.5	<0.3	1.5	<0.5
Stripper Overhead	<0.5	<0.5	<0.3	1.86	<0.5
<u>Company No. 200</u>					
Feed	<0.5	<0.5	<0.3	<0.1	<0.5
Stripper Overhead	<0.5	<0.5	<0.3	<0.1	<0.5
Stripper Bottoms	<0.5	<0.5	<0.3	<0.1	<0.5
<u>Company No. 400</u>					
Feed	<0.02	<0.2	<0.1	<0.02	<0.2
<u>Company No. 500</u>					
Feed	<0.02	<0.2	<0.1	<0.02	<0.2
<u>Company No. 600</u>					
Feed	<0.02	<0.2	<0.1	<0.02	<0.2
<u>Company No. 700</u>					
Feed	0.045	<0.2	<0.1	<0.02	<0.2

* (<) Indicates figure is lowest detectable limit of instrument used for analysis.

Process Effluent from Company 200

An additional 1.2 m of packing was added to the pilot steam stripper. Runs 12 through 14 were made on the modified unit (3.4 m packing). The packing material was changed from 6 mm (1/4 inch) Rasching rings to 16 mm (5/8 inch) Pall rings to improve vapor liquid contact and to achieve larger loading with the same diameter (7 cm) column. Results from runs 12-14 indicated that the residual methanol in the bottoms of the steam stripper ranged from 34 to 383 mg/l and the ammonia ranged from 80 to 160 mg/l. The high bottom concentrations corresponded to the 2.5% overhead runs and the low concentrations to the 14% overhead. Results of these three tests clearly indicated that one run through 3.4 m of packing was not enough to effect the desired removals (less than 20 mg/l) of methanol and ammonia. This column height deficiency could be made up by the addition of reflux. (Reflux is a term used when a portion of the condensed overhead is returned to the stripping column, as shown in Figure 2). Addition of reflux to a column theoretically adds packing height.

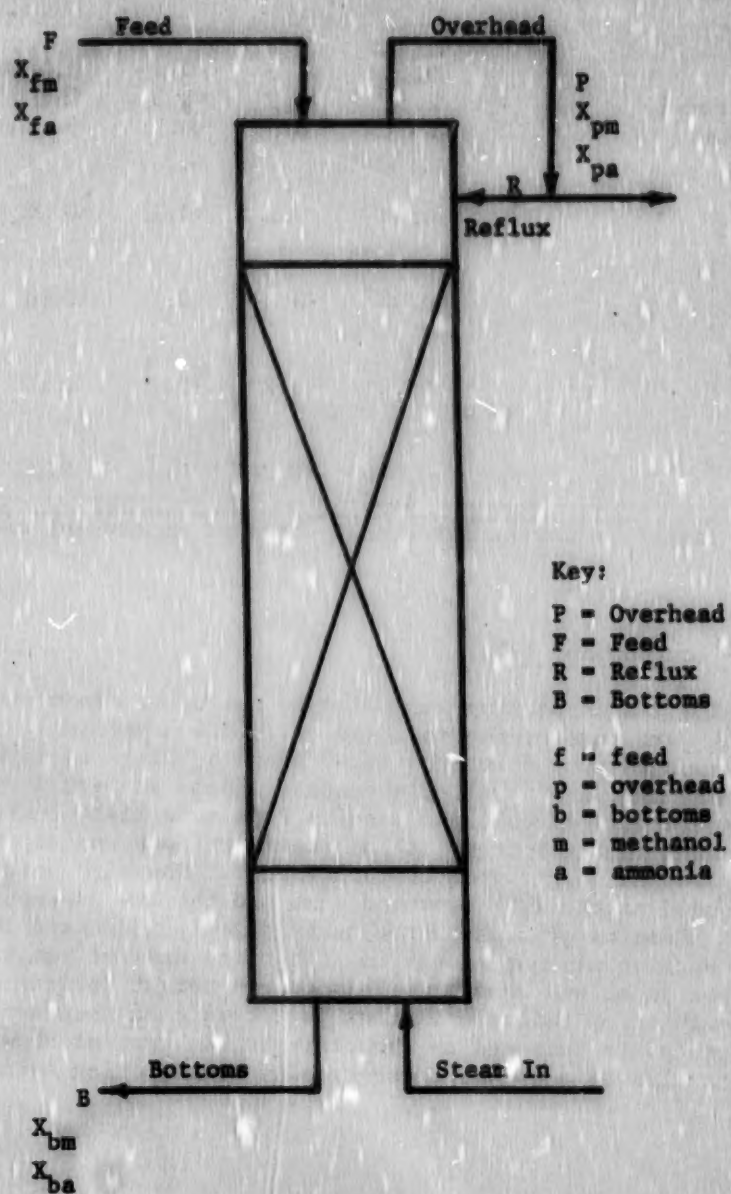


Figure 2. Mass balance equations with reflux.

Runs 15-18 were made on the bench stripper without the addition of reflux. Contaminants in the stripper bottoms from these tests were from 1 to 85 mg/l methanol and from 50 to 160 mg/l ammonia. The reduction of these two contaminants in the stripper bottoms was dependent on the percent overhead-to-feed ratio. For example, if the feed rate of process condensate to the steam stripper was 100 kg/min, then 10 kg of condensed overhead would represent 10%, and 5 kg/min condensed overhead would represent a 5% overhead rate.

Test runs 19-28 were conducted with a portion of the overhead refluxed. These tests did not give satisfactory results because the reflux pump did not function properly.

Runs 29 and 31 were without reflux, while runs 30 and 32 were with reflux. In these runs, ammonia in the stripper bottoms was reduced to very low limits (<5 mg/l). The percent overhead-to-feed ratio used to achieve these results was quite high (>10%). For example, a typical 907 m. ton/day plant generally produces about 45,000 kg/hr. If this 45,000 kg/hr is fed to a steam stripper, enough steam must be added to produce the desired overhead-to-feed ratio. If a 10% overhead rate is needed for this separation, then enough steam is added to vaporize 4,500 kg/hr (total) of water, ammonia, methanol and carbon dioxide. If these stripped overheads are reinjected into the primary reformer furnace, the amount of overhead generated (for reinjection) from the steam stripper affects the amount of energy required for condensation, pressurizing, re-evaporation, and injection into the primary reformer furnace for reclaiming of ammonia and methanol. In order to decrease this overhead rate and still achieve the desired separation (<20 mg/l ammonia and methanol) in the stripped bottoms, either packing height or refluxing rate has to be increased.

Process Effluent from Company 300

Test runs 33, 34, 36, 38, and 39 were without reflux while runs 35 and 37 were with reflux. Runs 33-39 were performed with the overhead less than 5% of the feed rate. For test runs without reflux, the concentrations of the contaminants in the stripper bottoms ranged from 10 to 35 mg/l for methanol, and 25 to 53 mg/l for ammonia. For test runs with reflux, the concentrations of the contaminants in the stripper bottoms ranged from 1 to 7 mg/l for methanol and 29 to 39 mg/l for ammonia.

Process Effluent from Company 400

Test runs 40, 42, 44, and 46 were without reflux, and runs 41, 43, 45, and 47 with reflux. The amount of methanol in the stripper bottoms was influenced significantly by the addition of reflux. Methanol in the bottoms was 119-129 mg/l and ammonia, 73-145 mg/l, for runs made without any reflux. For runs with reflux, the methanol varied between 30 and 32 mg/l and the ammonia between 62 and 100 mg/l. With the addition of reflux, the reduction in concentrations averaged 25.7% for ammonia and 74.9% for methanol.

Process Effluent Condensate from Company 200

An effort was made in the final runs to perfect the stripping technique for operating the pilot steam stripping column. Test runs 48, 49, 51, 53, 55,

57, 59 and 60 were performed without reflux, while runs 50, 52, 54, 56, 58, and 61 were performed with the addition of reflux. An effort was made to keep the reflux ratio (R/P as shown in Figure 2) at approximately 1:1. Residual methanol concentration in the stripper bottom varied between 4 and 100 mg/l without reflux and between 1 and 53 mg/l with reflux. Residual ammonia concentration in the stripper bottom varied between 14 and 81 mg/l without reflux and between 12 and 55 mg/l with reflux.

It was determined that a 5 to 6% overhead rate was optimum for the pilot scale equipment and process conditions. Under these conditions, the methanol and ammonia concentrations in the stripper bottoms would be <15 mg/l and <20 mg/l, respectively.

Pilot (Bench) Steam Stripper Mass Balance

Mass balances were determined from the data collected during the operation of the bench steam stripper in order to validate the steam stripping data. These mass balances were determined for methanol, ammonia, and total mass flow rates. Standard deviation (sum of squares) was calculated for this data revealing $\pm 9.9\%$ for methanol, $\pm 12.2\%$ for ammonia and $\pm 7.0\%$ for a total mass balance around the stripper column.

Vapor Liquid Data

Vapor-liquid equilibrium data were determined for three of the sources of process condensate for use in comparative design calculation. The source stream and its vapor-liquid equilibrium can be represented by the following equations:

$$\begin{array}{ll} \text{Stream 200;} & y = 147(x) - 110 \\ \text{Stream 500;} & y = 123.5(x) - 456 \\ \text{Stream 600;} & y = 232(x) - 100 \end{array}$$

where y is the mole fraction NH_3 in the vapor and x is the mole fraction NH_3 in the liquid.

COMMERCIAL UNIT

Design of Commercial Ammonia-Methanol Steam Stripper

Design calculations were made for a steam stripper column using pilot plant vapor-liquid equilibrium data. Vapor-liquid data would help to establish the necessary depth of packing to reduce the ammonia and methanol content to the specified level.

In the design calculations, both stripper columns using reflux and steam stripping without reflux were considered. Economic considerations would determine use and extent of reflux, which in turn influence packed bed depth and steam load to the stripper column. As stated earlier, refluxing theoretically increases the height of packing, depending on the reflux ratio used. However, refluxing uses more steam input because the portion of condensed overhead sent back to the column must be reheated and vaporized. Since

reflux requires more steam input, and since the diameter of the stripping column is determined by the liquid (feed)-vapor (steam) load, a high reflux could increase stripper column diameter. The following design conditions were used as the basis for a commercial size steam stripper.

1. 907 m. ton/day ammonia production.
2. 757 l/min process condensate wastewater stream with the following concentration.
 - a. Ammonia concentration of 1000 mg/l.
 - b. Methanol concentration of 750 mg/l.
3. Removals of 98% of the ammonia and 99% of the methanol showing the following concentration in the bottoms:
 - a. Maximum ammonia concentration of 20 mg/l.
 - b. Maximum methanol concentration of 5 mg/l.

Steam Stripper Overhead Disposal

There were four potential options investigated for disposal of the steam stripper overheads:

1. Reinjection
2. Precipitation with magnesium phosphate
3. Adsorption by vanadium pentoxide
4. Injection of the stripper overhead into the reformer stack

Several large ammonia producers have installed process condensate steam strippers which are discharging to the atmosphere. Analysis of the stripper bottoms indicates that this operation does reduce the ammonia in the stripper bottoms to the desired level. The net result, however, is that the contaminants have been removed from the water and redistributed into the surrounding atmosphere.

Economic Comparison of Treatment Schemes

Four processes were economically evaluated (January 1977 figures) for their cost effectiveness in reducing the ammonia and methanol present in the process condensate (Table 3). Ten-year straight-line depreciation with 8% interest charges were utilized for comparison. The cost-benefit ratio of stack injection outweighs other systems. The ammonia and methanol contained in the overheads from the stripper are reduced by 59.3 and 74.7 percent, respectively, with an increase of NO_x in the final stack emission of 95.3 kg/hr.

TABLE 3. ECONOMIC EVALUATION OF TREATMENT SCHEMES

	Atmospheric Steam Stripping With Stack Injection	With Reformer Injection	Vanadium Pentoxide Adsorption	Magnesium Phosphate Precipitation
Variable Cost	\$368,000	\$814,500	\$ 890,500	\$1,380,000
Fixed Cost	62,000	134,400	348,400	325,400
Total	430,000	984,900	1,238,900	1,705,300
Recovered Credit	None	61,000	61,000	288,000
Total Annual Cost	\$430,000	\$887,900	\$1,177,900	\$1,415,300
Cost per Liter	\$0.0012	\$0.0026	\$0.003	\$0.004
Cost/m. ton NH_3	\$1.49	\$3.20	\$3.94	\$4.41

Evaluation of Commercial Steam Stripper with Overhead Injection into the Reformer Furnace Stack

The commercial column was designed with 9.1 meters of stripping section packed with Pall rings. The stripper's overhead line was injected into the furnace stack approximately 8 meters above ground level. Total stack height measured 32 meters. Component and material balances of the 65 tests are listed in Table 4.

TABLE 4. COMPONENT AND MATERIAL BALANCES FOR COMMERCIAL UNIT

	Ammonia mg/l kg/hr		Methanol mg/l kg/hr		Flow kg/hr
Feed	487	39.2	262	21.1	30,300
Overhead	4,750	37.9	2,610	20.8	7,980
Bottoms	7	1.3	3.4	0.3	81,200
Steam	-	-	-	-	8,680
Total		86.4		46.5	
Percent Reduction		96.8		98.8	

Furnace Stack Analysis--

According to the Gibb's free energy calculation, the decomposition of ammonia to nitrous oxide in the furnace stack is highly probable in the presence of oxygen. If 100% of the ammonia (37.9 kg/hr NH_3) out of the steam stripper were converted to nitrogen dioxide (NO_2) in the primary reformer furnace stack by the following equation:



then the 37.9 kg/hr of NH_3 would be converted into 102.6 kg/hr (260.7 ppm) of NO_2 (Table 5). However, 15.5 kg/hr of ammonia was detected at the primary reformer stack discharge. A reduction of 22.4 kg/hr or a decomposition of some 59.2% of ammonia was observed. Also found in the primary furnace stack discharge outlet was 5.3 kg/hr of methanol, a reduction of 15.6 kg/hr or a decomposition of 74.7% of methanol. However, an increase from 67.6 kg/hr (172 ppm) to 95.3 kg/hr (242 ppm) of nitrogen oxide was observed. This increase of 27.7 kg/hr (70 mg/l) or 40.9% in nitrous oxide can be related to the ammonia reduction observed.

If the 22.4 kg/hr decomposition of ammonia were converted into nitrous oxide, this would represent an increase of 60.7 kg/hr of NO_2 . Since only 27.7 kg/hr increase of NO_2 was found, some of the ammonia must have decomposed into N_2 and H_2 .

TABLE 5. FURNACE STACK ANALYSIS

Component	Furnace Outlet		Stripper Overhead		Primary Reformer Discharge	
	ppm	kg/hr	ppm	kg/hr	ppm	kg/hr
Ammonia	0.0	0.0	4750	37.9	39.3	15.5
Methanol	0.0	0.0	2610	22.4	13.4	5.3
NOx	172	67.2	0.0	0.0	242	95.3

Effectiveness of Ammonia and Methanol Removal Via Furnace Stack Injection—

Measurements of the concentration of methanol and ammonia exiting the furnace stack were compared to theoretical calculated values for the stripper overhead being discharged directly. Ground level concentrations for these two cases were also calculated. Results are shown in Table 6.

TABLE 6. AMMONIA AND METHANOL REMOVAL VIA FURNACE STACK INJECTION

	Emissions		Maximum Downwind Ground Level Concentrations
	lb/hr	g/sec	($\mu\text{g}/\text{m}^3$)
<u>Actual Measurements</u>			
Ammonia	34.1	4.28	12.8
Methanol	11.6	1.46	4.4
<u>If No Decomposition</u>			
Ammonia	83.6	10.56	31.6
Methanol	45.9	5.78	17.3

CONCLUSIONS

Several conclusions can be drawn from the laboratory and plant evaluations of the removal of ammonia from process condensate via steam stripping:

1. Steam stripping is a viable process for the reduction of ammonia and methanol in ammonia process condensate streams and will achieve established EPA guidelines.
2. Injecting the overheads from the steam stripper into the reformer furnace stack can effectively reduce the amount of ammonia and methanol discharge to the atmosphere.
3. In the commercial unit evaluated, it is possible to strip the condensate and recycle the bottoms to the boiler feedwater system. The bottoms could be used for cooling tower make-up without further treatment, depending on final ammonia and methanol concentrations.
4. Pilot plant data on steam stripping of ammonia plant process condensate compared favorably with data from a full-scale commercial unit tested in an ammonia plant.
5. Trace metal levels in the condensate will not present a problem in the recycle of stripped bottoms to the boiler feed water treatment system. Trace metals would not present any problem if the overheads from the steam stripper were recycled to the primary reformer furnace in the ammonia process.
6. The concentration of ammonia in the process condensate varies with the age of the primary reformer catalyst and severity of process conditions.
7. ReInjection of process steam stripper overheads into the primary reformer furnace would require a stripper bed with reflux for concentrating the overhead. A preheater would be required prior to injection in the primary furnace and/or a large heat increase in the primary furnace itself.
8. Comparison of alternate treatment schemes for the atmospheric reduction of ammonia and methanol showed that venting the steam stripper overheads via the reformer furnace stack was the least costly.

SECTION 3

BACKGROUND

With the creation of the Environmental Protection Agency and its mandate to set effluent guidelines for various industries, many ammonia producers in Louisiana began to investigate means of reducing ammonia and organics from the process condensate they were discharging. As late as 1973, efforts had been made by the Guidelines Division of the Environmental Protection Agency to set permissible levels of ammonia which could be discharged into receiving waters.

After making an industry survey, the Guidelines Division initially set the amount of ammonia which could be discharged from a plant process condensate as the equivalent of 50 kg/day, which represented an average concentration of 50 ppm in the process effluent from a 907 m. ton/day ammonia plant discharging an average of 757 l/min from the process area. Data for setting this maximum ammonia concentration were based on assuming removals over this maximum in adjoining process equipment.

U.S. AMMONIA PRODUCTION

As of 1975, approximately 16-million m. tons of synthetic ammonia were produced annually in the United States. This product was manufactured in 30 states in some 88 plants. Figure 3 shows the location of these plants. By 1977, an additional 2-million plus m. tons will be added to the manufacturing capability of the industry.

In general, ammonia production units are located in areas where there is abundant natural gas. This material forms the basic raw material for cracking and furnishes fuel for the manufacturing process. Because of the availability of natural gas in Louisiana and Texas, these two states produce over 50 percent of the anhydrous ammonia in the United States. Louisiana alone produces nearly 30 percent.

AMMONIA PLANT WASTEWATERS

The technology of cracking methane for hydrogen production and combining with atmospheric nitrogen to manufacture ammonia has advanced significantly in the past 10 years. Over 98 percent of the ammonia production in the United States is done by the catalytic steam reforming of natural gas (see schematic, Figure 4). Some wastewater is an unavoidable product of the manufacturing process of ammonia via natural gas cracking. There are several sources of the effluent from an ammonia production facility:



Figure 3. Ammonia plant locations.

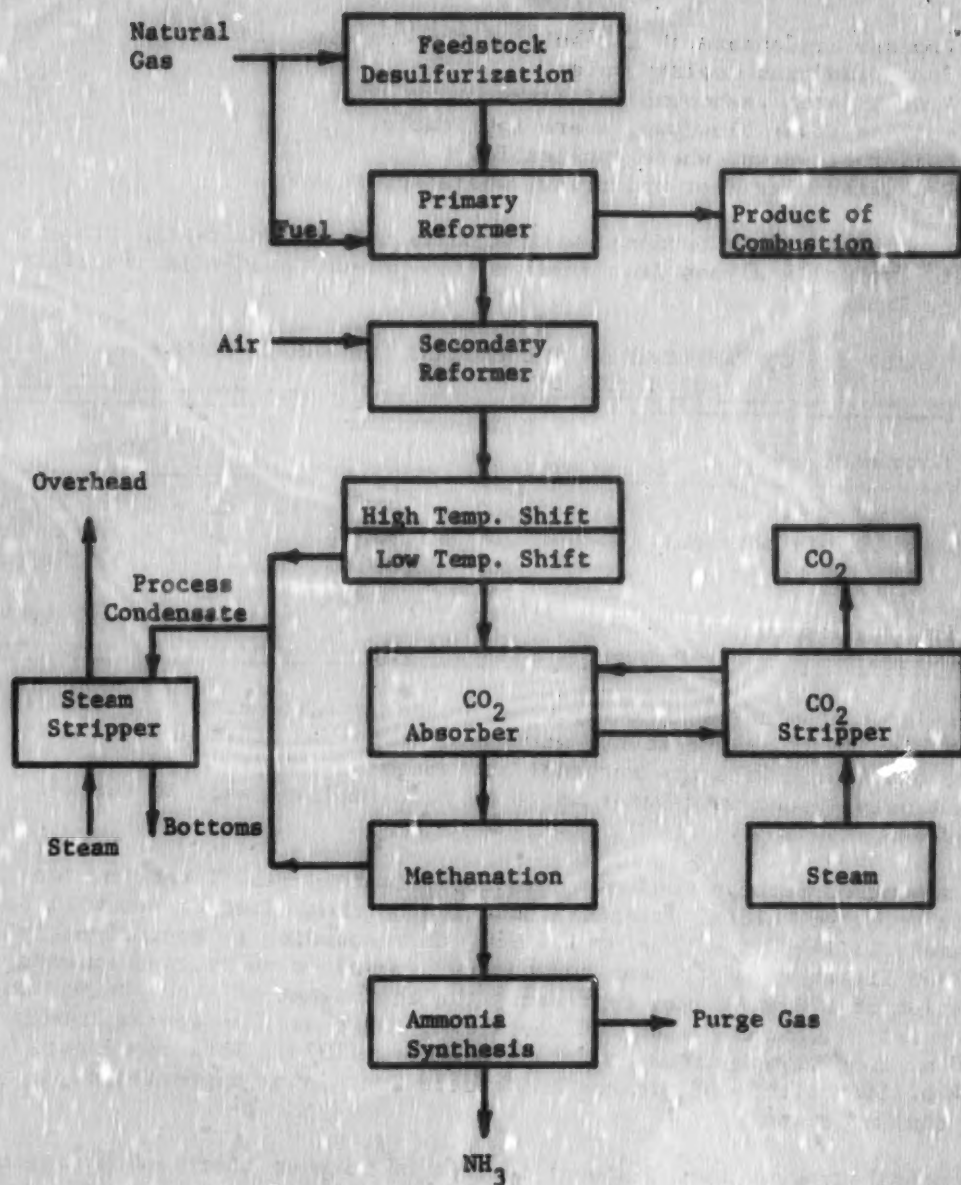


Figure 4. General process flow diagram of a typical ammonia plant.

1. Process condensate as a result of the cracking process.
2. Pump gland and sealant water.
3. Process area washdowns and leaks.
4. Cooling tower blowdown, where applicable.
5. Boiler blowdown, where applicable.
6. Raw water clarifier underflow, where applicable.

The wastewater most highly burdened with ammonia contaminant is the process condensate. Typical analyses from a 907 m. ton-per-day production facility are shown in Table 7.

TABLE 7. CONTAMINANTS IN THE PROCESS CONDENSATE FROM A
907 M. TON/DAY AMMONIA PLANT

Component	Concentration (mg/l)	Output
NH ₃	600 - 1,000	653 - 1,088 kg/day
Organics, mainly methanol	200 - 1,000	218 - 1,088 kg/day
CO ₂	200 - 2,800	218 - 3,039 kg/day
COD	200 - 1,200	
Process Condensate		600 - 757 l/min

The major contaminants in the process condensate are methanol, ammonia and carbon dioxide (CO₂). However, with respect to the effluents and emissions, the only pollutants are methanol and ammonia. CO₂ is a process contaminant only if the wastewater is to be reclaimed and used in further process areas.

The amount of process condensate is approximately 1150 liters/m. ton of ammonia produced. Total ammonia production in the United States will be approximately 18,144,000 m. ton/yr in 1980, corresponding to approximately 21.2 billion liters/yr of process condensate. Based on an average ammonia concentration of 800 mg/l, this represents the equivalent of about 16,950 m. tons per year. Within the State of Louisiana, there will be approximately 5,440,000 m. tons of anhydrous ammonia produced in 1978. This represents about 6.4-billion liters of process condensate containing approximately 5,400 m. tons of ammonia.

The possibility of land disposal instead of further treatment has been considered for this ammonia process condensate. Shipping and handling a product which is 95% water and 4% ammonia, methanol and other contaminants over long distance would be uneconomical. The possibility of using this condensate for crop irrigation is remote for Louisiana. However, if an ammonia plant were located in an area where this process water could be used for irrigation, and if 11.21 g/m² of ammonia per acre per season were needed, 116.9 liters/m² of process wastewater would be required. This would correspond to a square meter of land flooded to a depth of 12 cm with process water.

DEVELOPING NEW TECHNOLOGY FOR REMOVAL OF AMMONIA FROM PROCESS CONDENSATE WITH SUBSEQUENT RECYCLE

The only product from the majority of ammonia producers in Louisiana is anhydrous ammonia. Recognizing the need to develop technology which would be compatible with all EPA regulations, the ammonia producers, through their industrial membership in the Louisiana Chemical Association, participated in an EPA grant which was jointly supported by the following entities (see organization chart, Figure 5):

1. Louisiana State Science Foundation
2. U.S. Environmental Protection Agency, Industrial and Environmental Research Laboratory
3. Participating Companies through the Louisiana Chemical Association
 - a. Air Products and Chemicals, Inc.
 - b. American Cyanamid Company
 - c. Borden Chemical Company
 - d. C.F. Industries, Inc.
 - e. W.R. Grace & Company
 - f. IMC Corporation
 - g. Monsanto Company
 - h. Olin Corporation

The principal objective of the program was to establish technology to remove the environmental pollutants ammonia and methanol and the process contaminant carbon dioxide. Anticipating future effluent requirements, this program was designed to establish the technology to lower discharge of ammonia to the environment well below the EPA guideline of 50 kg/day and to minimize the discharge of methanol. The following program outline was developed.

1. Review previously developed information to evaluate possible technology transfer.
2. Evaluate steam stripping as a viable process.
3. Evaluate reflux of stripper overhead to concentrate ammonia.
4. Investigate disposal of ammonia concentrate.
 - a. Consider reinjection of concentrated stripper overhead into cracking furnace feed and the effect of this reinjection on increased furnace heat requirements.
 - b. Investigate injection of concentrated stripper overhead into furnace exhaust stack and the effect of stack temperatures on the decomposition of ammonia and methanol.
 - c. Study economics of adsorbing ammonia on vanadium pentoxide and subsequent recovery oxides.
5. Evaluate stripper bottoms as feed to:
 - a. Recycle to demineralize system.
 - b. Use directly in low pressure boiler.
 - c. Discharge into receiving waters.
 - d. Discharge in cooling tower make-up.
 - e. Recycle to water demanding process if available.

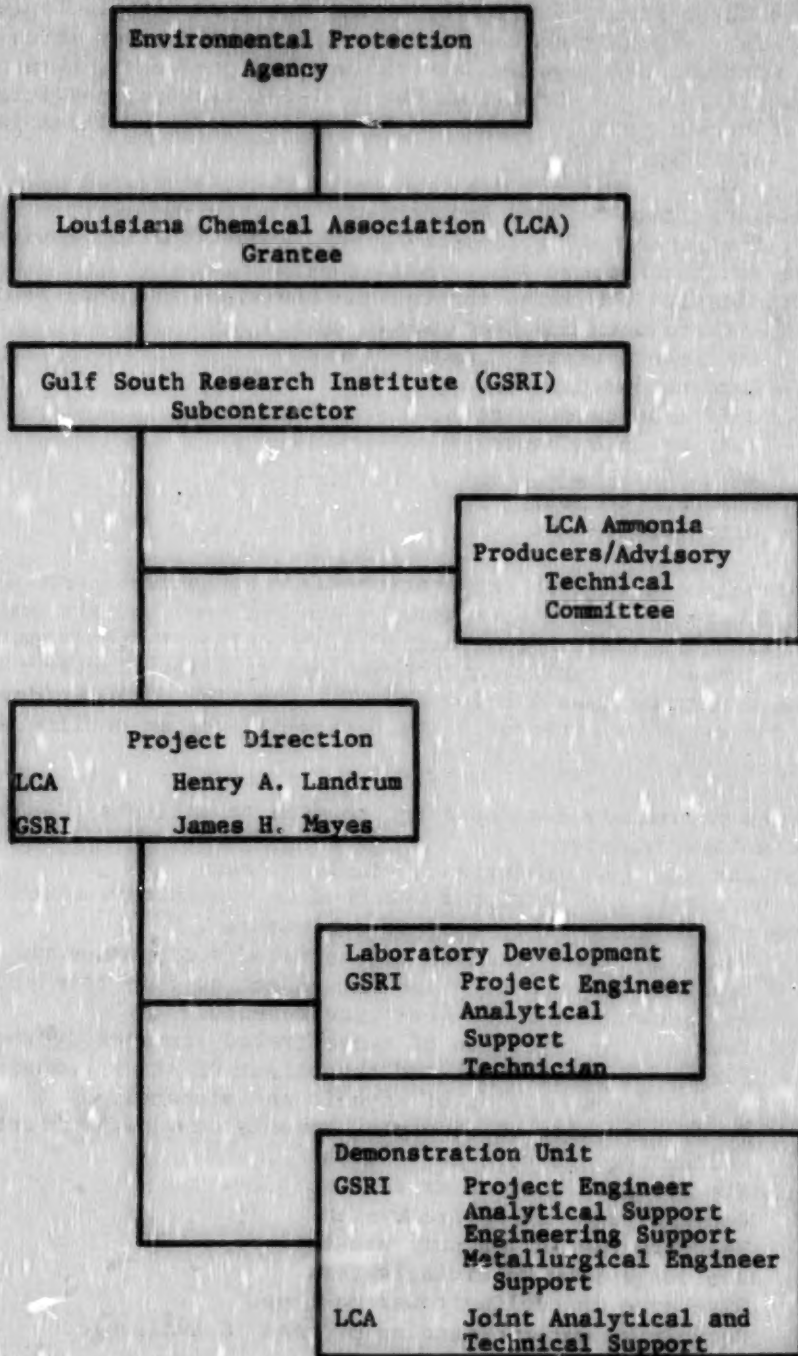


Figure 5. Organization chart.

SECTION 4

STATE-OF-THE-ART

Until several years ago, concentrations of nitrogen compounds in surface waters had not presented any serious problems due to excessive biostimulation (eutrophication). The microbial nitrification and denitrification of municipal wastewaters in conventional treatment plants was the primary means of keeping the nitrogen cycle in balance. Increased awareness of the impact of nitrogen entering the environment has led to investigations of other means of removal, particularly from more concentrated industrial sources, such as the process condensate from large ammonia plants. Some methods investigated were:

1. Microbial nitrification and denitrification.
2. Ion exchange.
3. Chlorination - dechlorination.
4. Ammonia plant process condensate steam stripping with air venting of stripper overhead.
5. Reverse osmosis.

None of these treatment systems offers an industry-wide solution to the reduction of the contaminant level in the ammonia plant process condensate effluent. Each will be discussed in turn to point out the limitations of industrial plant applications.

MICROBIAL NITRIFICATION AND DENITRIFICATION

Several modern ammonia plants treat their process condensate effluent with an aeration lagoon. Data from one such operation are shown in Table 8. Biological treatment under these conditions gives excellent reduction of methanol, but the ammonia is only partially reduced.

TABLE 8. PLANT TREATMENT OF PROCESS CONDENSATE

Component	Process Condensate Bio-Pond Influent (mg/l)	Bio-Pond Effluent (mg/l)
Ammonia	800-1100	100-650
COD	2200-2800	100-400
BOD	1600-2800	150-250
pH	8-9	8-8.5

It has been the practice of many treatment plants to convert nitrogen, in the form of ammonia, to nitrates through the process of nitrification(1). This oxidation of ammonia is performed by a specific group of microorganisms which have growth rates that are highly temperature-sensitive. In a study by Bingham, *et al.*(2), a pilot unit trickling filter was evaluated under laboratory conditions for the conversion of ammonia to nitrate. The results of this study indicated that ammonia removal was dependent on hydraulic flow rate, temperature, and inorganic carbon concentrations. Ammonia removal through the trickling filter amounted to 20 to 40 percent even at the best hydraulic loadings. Thus, even with good carbon conversion, the nitrification of ammonia would take considerable residence time or a number of trickling filters in series.

Under anaerobic conditions, microorganisms utilize chemically bound oxygen for the final hydrogen acceptors. Therefore, in an anaerobic environment, the nitrate from the nitrification treatment system may be reduced or denitrified to gaseous forms of nitrogen. This principle has been employed in previous investigations(2) for the removal of nitrate nitrogen from agricultural runoff. For proper denitrification, an organic carbon source must be present so that the microbes can perform their normal metabolic activities. Past investigations have indicated that methanol may be the most economical source of supplemental carbon(1). Thus, the presence of methanol in the ammonia plant process condensate effluent was initially regarded as encouraging for the biological approach to effluent treatment. Unfortunately, the concentration levels of the ammonia in the effluent were so high that satisfactory treatment could not be achieved in a reasonable length of time. Also, the addition of phosphates is necessary for the reactions to occur.

Considerable work was done by Bingham, *et al.*(2) on biological denitrification of effluent from an ammonia and ammonium nitrate plant at Farmers Chemical Association in Harrison, Tennessee. The ammonia and nitric acid plant effluent amounted to 2.7×10^6 liters per day and contained 100 mg/l of ammonia nitrogen and 120 mg/l of nitrate nitrogen. The ammonium nitrate plant effluent was 3.79×10^5 liters per day and contained 2500 mg/l ammonia nitrogen and 10,000 mg/l nitrate nitrogen. Based on the study by Bingham for denitrification of this stream, the optimum COD-to-nitrate ratio was 3.2:1 (about 6:1 methanol:nitrogen). The necessary retention period was 25 to 30 days.

Eckenfelder(3) discusses the relationship between residence time and temperature for the nitrification reaction. If the reaction temperature drops from 15° to 6°C, the residence time for the same level of nitrification will approximately double. (Estimates are based on nitrogen reduction in domestic sewage.)

According to data presented by Johnson(4), activated sludge plants show removals of organic nitrogen ranging from 50 to 85 percent and a total nitrogen removal of 16 to 75 percent. Johnson further states that the removal of nitrogen is a function of the BOD-to-nitrogen removal ratio and that an increase in the nitrogen content of an effluent would reduce nitrogen removal.

The often-used rule of thumb for domestic sewage is 15 mg/l organic nitrogen and 10 mg/l ammonia nitrogen. Obviously, in most activated sludge plants the organic nitrogen is biodegraded while the ammonia nitrogen remains essentially unchanged. Microbial nitrification-denitrification systems for ammonia contaminated process condensate effluents are limited by two additional drawbacks: (1) For high concentrations of ammonia-nitrogen, the retention times necessary to achieve realistic reductions are too great; the impounding of areas is a waste of valuable land. (2) During winter operation (lower temperatures), treatability levels would fall below acceptable standards.

SELECTED ION EXCHANGE

In other research, Bingham, et al.(5) concluded that ion exchange offered the best solution to the ammonia and nitrate removal from the effluent from the Harrison, Tennessee, plant. Supporting this conclusion was an extensive investigation of various methods of reducing nitrogenous compounds in the Farmers Chemical Association plant. The research and development program was supported and financed in part by the United States Environmental Protection Agency. The following processes were investigated:

1. Biological nitrification.
2. Biological denitrification.
3. Stripping of ammonia.
4. Precipitation of ammonia as magnesium ammonium phosphate.
5. Recovery of ammonium nitrate by reverse osmosis.
6. Recovery of ammonium nitrate by continuous ion exchange.

Bingham, et al.(5), summarized their conclusions regarding the above treatment processes as follows:

1. Microbial nitrification of ammonia nitrogen in plant effluents over laboratory and plant scale trickling filters was inefficient (indicating inadequate residence time) and temperature sensitive.
2. Biological denitrification of nitrate nitrogen in plant effluents under laboratory and plant scale anaerobic conditions in stabilization ponds also proved ineffective.
3. Air stripping of ammonia nitrogen under laboratory and plant-scale conditions showed promise. (Stripped by-product was vented to atmosphere.)
4. Precipitation of ammonia nitrogen as magnesium ammonia phosphate showed promise if the treatment process could be integrated into existing operations.
5. Ion exchange apparently would provide effluent water of adequate quality for reuse or discharge.

To achieve success with the ion exchange system, the recovered by-product, ammonium nitrate, would have to be concentrated and added to the finished product of the plant. Potential features of the treatment system included:

1. Use of both nitric acid and ammonium hydroxide as regenerants on cation and anion units since both these compounds are in-plant products and thus are preferred regenerants.
2. Use of strong acid cation exchange resins and weak base macroreticular anion exchange resins.
3. High total dissolved solids as calcium carbonate.

Farmers Chemical Association had a plant producing ammonia and nitric acid which were subsequently converted to ammonium nitrate by evaporation and drying. The ion exchange regeneration products could be charged to the product evaporation units. The regenerant stream from the ion exchange beds contained 85% water. A considerable capital investment was necessary to concentrate this stream. For operation of the ion exchange unit, it was necessary to utilize about twice the amount of regenerant chemicals (nitric acid and ammonia) present in the effluent. Thus, the process is not economically attractive.

CHLORINATION-DECHLORINATION

In a study by Atkins and Schegner(6) sponsored by the EPA, the feasibility of using chlorination followed by dechlorination with granular activated carbon for the removal of ammonia nitrogen from effluent water was demonstrated. This study was conducted on a domestic sewage effluent with an average concentration of 300 mg/l ammonia nitrogen. Several findings of this study were:

1. The ammonia removal process tends to depress the pH in nonbuffered systems and might necessitate adjustment of the final effluent.
2. The chloride content of the wastewater was increased from 193 mg/l to 293 mg/l.
3. Dissolved oxygen levels of the final effluent were between 1 and 2 mg/l, necessitating re-aeration.
4. Complete removal of ammonia nitrogen from wastewater required a chlorine-to-ammonia feed rate of 9-to-1.
5. If pretreatment is inadequate, considerable chlorine will be consumed by other impurities in the water, increasing both chlorine and activated carbon cost.
6. High ammonia nitrogen contaminated effluents would create excessive chloride concentrations in the final effluent.

The chlorination-dechlorination process offers excellent treatment possibilities for waste streams which have ammonia nitrogen concentrations within the order of magnitude of domestic sewage (300 mg/l average). Streams contaminated with higher ammonia nitrogen concentrations (i.e., 1000 mg/l) present economic and chloride contamination problems.

AMMONIA STRIPPING

Several investigators have studied the aeration of aqueous effluent for the removal of ammonia(7-9). The important criteria appear to be pH, air-

to-water ratio, and contact time. Stripping towers for the treatment of process condensate have proven effective at several plant installations; however, all of these systems are vented to the atmosphere. The best removal in aeration columns, reported by Rohlich(7), was 92% at pH of 11, an air-to-water ratio of 500, and a packed bed depth of 2.1 m. Less bed depth led to serious reduction in efficiency and aeration rate; at a lower pH, efficiency should be less due to the formation of ammonium ions. Culp and Selechta(8) have reported removals of ammonia up to 80% at pH of 9.3 and 98% at pH of 10.8 at air-to-water ratios of 800 and a contact time of 0.5 min. Other than the steam-stripping proposed by Kellogg (10), no research has been reported on the stripping of an ammonia-methanol aqueous mixture.

REVERSE OSMOSIS

It would be possible to develop a membrane to remove ammonia from water. However, several factors would have to be evaluated: (1) the cost effectiveness of the process, (2) the disposal of the resulting ammonia solution if only anhydrous ammonia is produced, and (3) the relationship of the methanol present in the condensate to the reverse osmosis action. To date, no development program has been initiated to investigate the commercial potential of removal of ammonia by membrane action.

EFFECT OF VARIOUS TREATMENT PROCESSES ON REMOVAL OF NITROGEN COMPOUNDS

The effect of removal of nitrogen compounds by the previously discussed process method is shown in Table 9. These values are averages from the literature.

TABLE 9. EFFECT OF VARIOUS TREATMENT PROCESSES ON NITROGEN REMOVAL

Treatment Process	Removal of Total Nitrogen (%)
Biotreatment	10 to 20
Reverse Osmosis	50 to 90
Dialysis	30 to 60
Breakthrough Chlorination	80 to 90
Ion Exchange	80 to 95
Ammonia Stripping	80 to 90

SECTION 5

CHARACTERIZATIONS OF AMMONIA PLANT PROCESS CONDENSATE

CONTAMINANT IDENTIFICATION

The participating companies represented seven different plant process condensate sources. Each stream was analyzed for ammonia, methanol and carbon dioxide. Results of several samples of each stream were averaged and are presented in Table 10.

TABLE 10. METHANOL, AMMONIA, AND CARBON DIOXIDE CONCENTRATIONS

Stream Number	Ammonia (mg/l)	Methanol (mg/l)	Carbon Dioxide (mg/l)
100	800	459	1137
200	1041	362	2470
300	858	618	2579
400	1015	972	2789
500	825	559	1258
600	700	172	642
Average	873	524	1809

A review of stream characterization data indicated that stream 700 was too low in ammonia, methanol, and carbon dioxide concentration to be classified as a representative sample stream. Therefore, values for stream 700 are deleted. Table 10 shows concentration of the three contaminants from representative streams, the average values being ammonia, 873 mg/l; methanol, 524 mg/l; and carbon dioxide, 1809 mg/l. Age of the catalyst and severity of operations affect the amount of each of these contaminants. However, the ratio of the three remains fairly constant. The ratios of methanol and carbon dioxide to ammonia are shown in Table 11.

TABLE 11. RATIO OF AMMONIA-TO-METHANOL-TO-CARBON DIOXIDE

Stream Number	Ammonia	Methanol	Carbon Dioxide
100	1.0	0.57	1.42
200	1.0	0.35	2.37
300	1.0	0.72	2.98
400	1.0	0.96	2.35
500	1.0	0.68	1.52
600	1.0	0.25	0.92
Average	1.0	0.58	1.99

TRACE METAL ANALYSES OF THE PROCESS EFFLUENT

There are two areas of concern regarding trace metals: recycling of stripper overheads to the process and recycling of stripper bottoms to the boiler water system. Trace metals in the feed stream could poison the catalyst system on the process side and might cause problems on the steam generation side. Samples of condensate from each of the participating companies were analyzed, with the results shown in Table 12. As a further check on where the metals in the process condensate would go is the stripping operation, runs from the bench-scale operation were sampled. These results are shown in Table 13. Levels of trace metals in the process condensate detected (or below the detection limit of the instruments used) would not present problems with regard to further processing or recycle.

TABLE 12. METAL ANALYSES

Sample I.D.	Cu (mg/l)	Ni (mg/l)	Fe (mg/l)	Zn (mg/l)	Cr (mg/l)
<u>Company No. 100</u>					
Feed	<0.5	<0.5	<0.3	1.5	<0.5
Stripper Overhead	<0.5	<0.5	<0.3	1.86	<0.5
<u>Company No. 200</u>					
Feed	<0.5	<0.5	<0.3	<0.1	<0.5
Stripper Overhead	<0.5	<0.5	<0.3	<0.1	<0.5
Stripper Bottoms	<0.5	<0.5	<0.3	<0.1	<0.5
<u>Company No. 400</u>					
Feed	<0.02	<0.2	<0.1	<0.02	<0.2
<u>Company No. 500</u>					
Feed	<0.02	<0.2	<0.1	<0.02	<0.2
<u>Company No. 600</u>					
Feed	<0.02	<0.2	<0.1	<0.02	<0.2
<u>Company No. 700</u>					
Feed	0.045	<0.2	<0.1	<0.02	<0.2

TABLE 13. PRELIMINARY RESULTS OF HEAVY METAL ANALYSES ON GRAB SAMPLES

Metal	R-27, 28 Feed (mg/l)	R-29 Overhead (mg/l)	R-30 Overhead (mg/l)	R-23 Bottom (mg/l)	R-70 Bottom (mg/l)
Cu	<0.5	<0.5	<0.5	<0.5	<0.5
Zn	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	<0.5	<0.5	<0.5	<0.5	<0.5
Cr	<0.5	<0.5	<0.5	<0.5	<0.5
Pb	<0.3	<0.3	<0.3	<0.3	<0.3

Several samples of process condensate were analyzed for the presence of methylamines, and none were detected. In order to verify that the gas chromatograph (GC) was capable of detecting methylamines, a gas sample of methylamine was received and tested. It was concluded that methylamine was not present in the process condensate. A mass spectrometric analysis confirmed that methylamines were not present in the process condensate.

SECTION 6

DEVELOPMENT OF STRIPPING DATA FROM LABORATORY AND BENCH-SCALE DATA

INTRODUCTION

As indicated in the stream characterization section, the average values for the three contaminants were: ammonia 873 mg/l, methanol 524 mg/l and carbon dioxide 1809 mg/l when the lowest stream analysis was omitted. Streams 100, 200, 300, and 400 were thought to be more representative of the level of contaminants to be found in the ammonia process condensate. It was decided to perform bench-scale tests on these streams.

A technology review indicated that steam stripping of the process condensate would reduce the ammonia and methanol contaminants. However, there were several questions concerning the stripper operations if the overhead were condensed for reinjection into primary reformer process.

- If the overhead were condensed, would the methanol and ammonia form a second phase?
- Would the carbon dioxide form a carbonate product with the ammonia?
- Would the stripper remove the desired amount of contaminants?

BENCH-SCALE STREAM STRIPPING OF PROCESS CONDENSATE

A bench-scale unit was constructed to clarify operating conditions for the steam stripper with condensation of the overhead and subsequent reinjection into the primary reformer. Drum samples of process condensate from several different plants were transported to the laboratory unit for test runs. The laboratory staff operated the small column, obtaining analytical data for interpretation and operational changes.

The pilot steam-stripper system is depicted schematically in Figures 6 and 7. The column was made from a 7 cm diameter piece of Derakane, with an overall length of 4.3 m. Packing height was 3.4 m with 1.6 cm (5/8 inch) polypropylene Pall rings as the fill material. Feed was measured to the system through a calibrated rotameter, and a peristaltic pump was used for flow continuity. Steam for stripping was preset by a needle valve and measured by a calibrated orifice. To minimize all process losses, the bottom and overhead were condensed in a refrigerated bath.

Analytical Techniques

Analyses of the process condensate from the participating industries and from the pilot steam-stripper for ammonia, methanol, methylamines, and



Figure 6. Pilot steam stripper located
at CSRI, New Orleans.

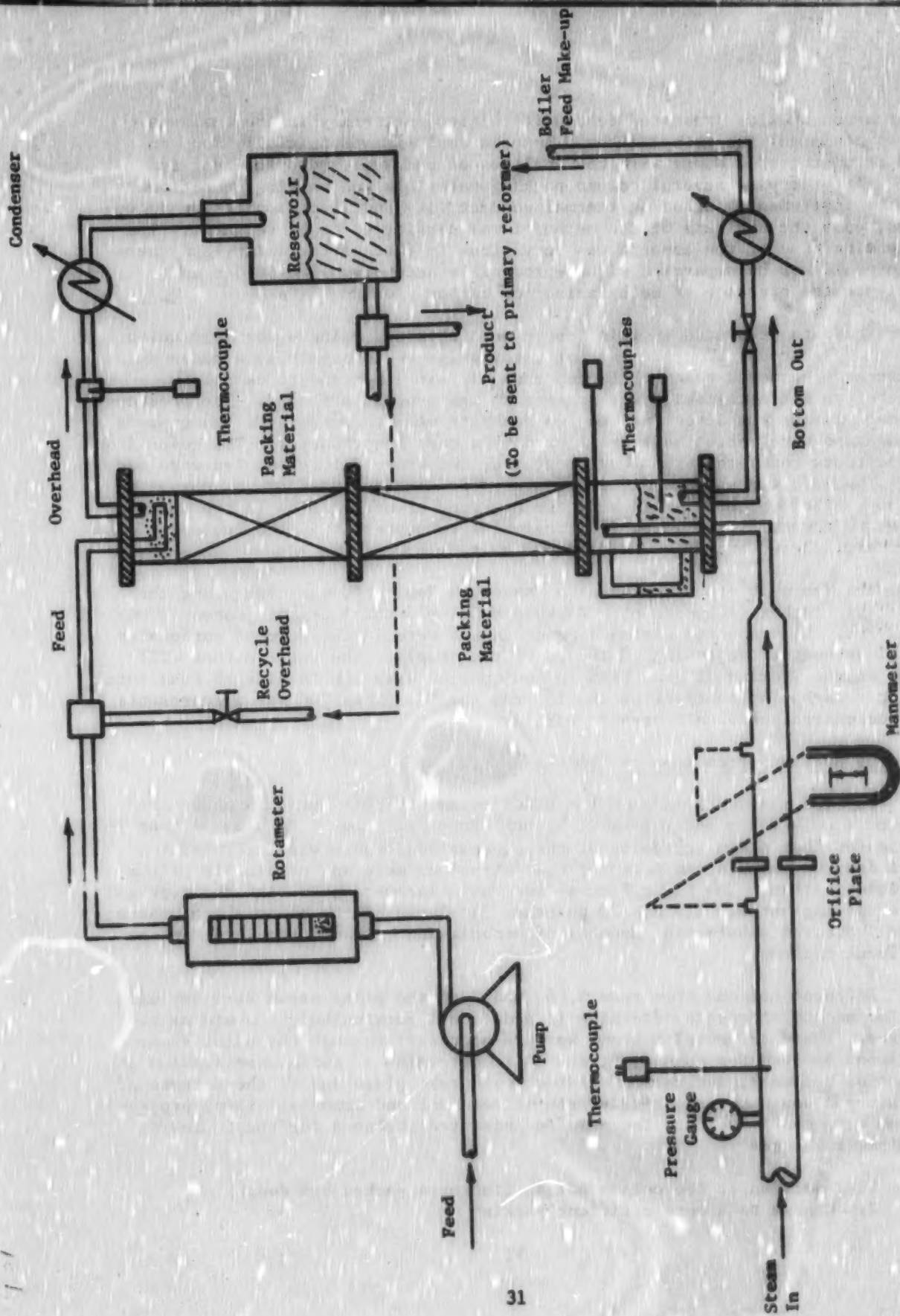


Figure 7. Model of pilot steam stripper (Gulf South Research Institute - New Orleans).

and carbon dioxide presented some difficulties, primarily in the analysis of the ammonia and the methylamines. Ammonia analysis was initially done on a gas chromatograph, along with the analyses of methanol, methylamines, and CO_2 . After trying several column packing materials and varying conditions of the instrument, including thermal conductivity and flame ionization detectors, only the analysis of the methanol was considered to be reliable. The retention time of the ammonia was very close to that of the water, and therefore could not be separated with reproducible accuracy. The GC did not indicate the presence of methylamines or carbon dioxide.

The data presented in this report were obtained using a specific anion ammonia electrode. The presence of methylamine could result in erroneous answers for ammonia concentrations, thus it was important to establish whether or not methylamine was present in the process effluent. The presence of methylamine was determined by two separate means. Samples of the process condensate were collected and analyzed by a mass spectrometer. The results of these tests for methylamine were received, and known dilute samples were made up. These spiked samples of methylamine were then analyzed by gas chromatography. The GC analysis did show the presence of methylamine in the amount added to the samples. Thus, if methylamine were present in the process effluent, the GC analysis would identify it.

The analysis of carbon dioxide, shown in Table 14, was done using the inorganic carbon (IC) side of a Beckman Model 915 total organic carbon (TOC) analyzer. All reported carbon dioxide values were in the form of carbonates or bicarbonates, depending on the pH of the sample. The total carbon (TC) side of the Beckman 915 was used in conjunction with the IC side to find total organic carbon by subtracting the IC from the TC. This TOC value represents the concentration of all organic carbons.

Process Effluent from Company 100

Initial runs were made on the pilot steam stripper having a packed bed depth of only 2.2 m and 0.6 cm (1/4 inch) Rasching rings. Results of runs 1-7 indicated that steam stripping of the process condensate was feasible, but that desired ammonia and methanol concentrations were not attainable in the effluent bottom. The first 7 runs (see Table 14) were made with the overhead rate varying between 2.5 and 20 percent. Analysis of the bottoms from these runs indicated substantial amounts of ammonia and methanol remaining in the effluent bottoms.

Effluent bottoms from runs 5, 6, and 7 of the pilot steam stripper were collected and stored to determine if additional packing height would be required. These collected bottoms were re-processed through the pilot steam stripper as feed for runs 8, 9, and 10 to determine if further separation of ammonia, methanol, and carbon dioxide would take place and if the bottoms of this rerun would be essentially free of methanol and ammonia. These projections were confirmed, and the results indicated the need for the following equipment changes:

1. Addition to the column height (increase packed bed depth)
2. Change to a more efficient packing

TABLE 14. ANALYSES FOR METHANOL-AMMONIA-CARBON DIOXIDE ACQUIRED BY STEAM STRIPPING IN BENCH SCALE UNIT

Run No.	Overhead Rate ml/min	Bottom Rate ml/min	Feed Rate ml/min	Reflux Rate ml/min	Steam Rate kg/hr	Feed mg/l NH ₃	CO ₂	Overhead mg/l Meath	HE ₃	mg/l CO ₂	Bottoms mg/l Meath	HE ₃	mg/l CO ₂	Feed Overhead Bottoms TOC mg/l	TOC mg/l	Bottoms TOC mg/l	
Runs 1-11 on Company No. 100																	
1	20.0	250	220	-	3.22	1174	620	1450	17980	6600	18000	193	180	186	1174	17987	381
2	19.0	185	170	-	3.83	1040	580	1600	7096	5200	9595	43	60	136	1028	10336	64
3	8.0	185	170	-	2.61	1040	580	1600	17740	6500	17000	171	98	135	1028	13763	254
4	4.5	185	170	-	2.17	1040	580	1600	16450	9700	25824	171	90	166	1028	14976	232
5	34.0	200	165	-	4.17	1526	2700	1548	3333	2000	1595	20	25	53	1235	4312	69
6	18.0	197	165	-	2.86	1526	2700	1548	10443	2700	8452	64	54	98	1235	10400	152
7	28.5	200	165	-	2.17	1526	2700	1548	16443	5600	12162	173	110	172	1235	16330	384
8	28.5	230	195	-	3.22	89	65	342	613	580	1369	7	7	15	397	1436	57
9	19.0	230	195	-	2.38	89	65	342	774	600	1672	14	8	21	397	1685	71
10	11.0	220	195	-	1.88	89	65	342	1422	570	2097	32	9	14	397	2360	81
11	5.0	340	300	-	3.36	1422	570	2097	57000	10400	22218	444	240	640	1229	38120	813
Runs 12-32 on Company No. 200																	
12	28.0	250	220	-	3.47	581	900	2816	5345	4000	8569	34	80	158	834	7077	61
13	16	250	220	-	3.22	581	900	2816	6451	3300	14501	92	140	264	834	7890	107
14	6.0	245	220	-	2.17	581	900	2816	10160	19500	40326	383	160	667	834	13205	304
15	18	395	260	-	4.76	257	1200	3399	8063	22000	32838	16	40	87	680	11168	32
16	5.2	390	360	-	3.63	257	1200	3399	21200	15000	111228	85	160	272	680	25912	173
17	22	450	392	-	5.22	280	1100	3381	7653	10000	28174	-	50	66	579	10416	29
18	19	450	390	-	4.99	280	1100	3381	9358	22000	34393	-	62	105	579	12405	40
19	8	500	390	58	4.99	280	1100	3381	25112	60000	126309	69	140	270	579	32704	123
20	40	410	320	68	5.44	280	1000	3263	6519	20000	14571	-	19	39	664	8707	29
21	26	420	320	68	4.85	280	1000	3263	16965	49000	52546	-	54	97	664	16256	38
22	30	475	360	68	5.44	253	1150	3227	10456	29000	42555	-	45	76	661	12389	37
23	14	495	360	68	4.85	258	1150	3227	5729	49500	45819	35	100	161	661	59744	73
24	26	400	360	-	4.85	258	1150	3227	23122	19000	27199	-	29	52	661	8090	28
25	53	420	375	-	6.03	260	1000	3157	3143	9500	13827	-	11	21	629	4083	23
26	26	375	375	35	6.03	260	1000	3157	5788	16500	16500	-	15	28	629	7536	22
27	47	355	260	108	5.89	300	1200	3212	10158	37500	39757	-	9	21	59	12509	27
28	64	385	260	108	6.35	300	1200	3212	9454	28500	31405	-	6	14	59	11291	22
29	30	260	260	-	3.04	317	1100	3131	2889	8000	15396	-	4	11	648	4920	171
30	45.5	260	260	25	4.76	317	1100	3131	3699	10000	16966	-	5	11	648	4547	19
31	34	260	260	-	3.36	317	1100	3131	2461	13000	13200	-	1	10	648	4539	19
32	58	272	260	42	5.21	317	1100	3131	3076	9000	75438	-	4	7	648	4445	19

(continued)

TABLE 14 (continued)

Run No.	Overhead Rate ml/min	Bottom Rate ml/min	Feed Rate ml/min	Reflux Rate ml/min	Steam Rate ig/hr	Feed NH ₃ mg/l	Meth	CO ₂	Overhead NH ₃ mg/l	Meth	CO ₂	Bottoms NH ₃ mg/l	CO ₂	Feed Overhead Bottoms TOC mg/l	TOC mg/l	Bottoms TOC mg/l	
Runs 33-39 on Company No. 300																	
33	16.8	380	350	-	3.90	615	825	2763	14646	18000	28549	10.6	25.2	40	765	13109	64
34	13.4	390	360	-	3.90	615	825	2763	17498	21500	39358	23.4	53.0	37	765	16272	59
35	46.5	430	360	34	5.44	615	825	2763	24693	27750	34943	1.0	29.0	18	765	21461	24
36	12	380	340	-	3.90	621	890	2354	20914	25000	47271	35.5	33.0	37	739	19232	72
37	39	420	340	29	5.44	621	890	2354	18908	31250	35926	1.0	39.0	18	739	18485	53
38	15	350	310	-	3.90	621	890	2354	14771	27750	39953	7.3	43.0	18	739	15961	56
39	27	345	310	-	4.35	621	890	2354	7320	26250	17739	1.0	35.5	11	739	8251	21
Runs 40-47 on Company No. 400																	
40	11	395	350	-	3.90	1143	1000	3260	38205	21250	61028	108	142	48	1754	38624	139
41	44	430	350	28	5.44	1143	1000	3260	35518	23000	45305	3.3	96.0	26	1754	35925	45
42	9	430	395	-	3.90	1134	1060	3260	46433	23500	80681	122	145	59	1696	40074	131
43	40	460	395	30	6.12	1134	1060	3260	47035	30000	60045	6	100	29	1696	46688	40
44	12	360	345	-	3.36	805	1000	2390	24400	26250	29381	119	73	286	652	8013	78
45	32	380	345	25	5.13	805	1000	2390	35138	37000	36186	30	74	-	652	9868	-
46	8.6	330	320	-	2.68	805	1000	2244	22578	31000	26427	128	80	280	612	6662	77
47	28	350	320	19.2	3.90	805	1000	2244	27745	32750	31104	32	62	117	612	8483	32
Runs 48-61 on Company No. 200																	
48	5.5	350	330	-	3.36	448	1000	1888	17626	40000	23870	100	67	158	515	6510	43
49	11.8	350	300	-	3.63	448	1000	1888	11602	30500	16710	64	81	213	515	4012	50
50	30	395	380	24.6	3.95	448	1000	1888	16101	37750	21120	11	55	125	515	5761	34
51	11.6	320	260	-	2.89	397	930	1521	3400	11000	9190	23	38	137	415	2506	37
52	23.2	323	260	11.8	3.63	397	930	1521	9162	19000	15240	53	22	92	415	4157	25
53	15.5	365	310	-	3.63	397	930	1521	7097	19200	15858	16	27	95	415	4325	26
54	32.2	385	310	16	3.95	397	930	1521	7582	18900	14180	4	15	91	415	3068	25
55	17.3	385	350	-	3.95	448	880	1532	7523	16675	14900	4	14	110	418	4065	30
56	13	400	350	17.3	5.44	448	880	1532	7825	21500	11970	1	12	48	418	9265	13
57	7	300	255	-	2.68	454	1100	1595	13917	32250	52	42	143	415	4061	56	39
58	14	310	255	7.6	3.63	454	1100	1595	14356	28750	14061	25	41	205	415	4001	56
59	4.3	290	210	-	3.63	454	1100	1595	7291	17750	12000	4	19	136	435	3271	37
60	9.9	370	320	-	3.63	429	968	1525	11450	28750	15300	30	32	132	416	4173	36
61	19.6	380	320	11.0	4.67	429	968	1525	13216	29375	19375	29	27	147	416	5284	40

3. Addition of a reflux system

With the modifications completed on the pilot steam stripper, a series of test runs was made on the unit. Tests were conducted at various feed, overhead, and reflux rates. Run 11 was performed on overheads collected from run 10. The data for these tests are presented in Table 14.

Process Effluents from Company 200

An additional 1.2 m of packing was added to the pilot steam stripper, making a total packed depth of 3.4 m. The packing material was changed from Raschig rings (6 mm) to Pall rings (16 mm). This type of packing has been proven to give better vapor-liquid contact with larger loading capabilities. It also enables for a more uniform vapor-liquid loading during the stripping operation. (The term vapor refers to the steam to the stripper column, and the term liquid refers to the process condensate feed to the pilot steam stripper.)

Results from first runs (12-14) made on the modified pilot steam stripper indicated that residual methanol in the bottoms of the steam stripper ranged from 34 to 383 mg/l and the ammonia ranged from 80 to 160 mg/l. The amount of overhead (2.5%) stripped from the feed in this test corresponded to the high bottom concentrations. The 14% overhead rate corresponded to the low concentration of the effluent bottom from the pilot steam stripper. Results of these tests indicated that once through 3.4 m of packing was not enough to effect the desired removals (less than 20 mg/l) of methanol and ammonia.

This column height deficiency could be made up by the addition of reflux. With reflux, a portion of the condensed overhead is returned to the stripping column, as shown in Figure 2. Reflux gives the column greater capability and flexibility and theoretically adds packing height to the column. However, the addition of reflux requires additional load on the overhead condenser and to the top of the column. Additional stripping steam would be required which would in turn increase the vapor-liquid load to the column. However, with reflux, the net result would be a decrease in the methanol and ammonia concentrations in the stripper bottom effluent.

Runs 15-18 were made on the bench stripper without reflux. Contaminants in the stripper bottoms from these tests were from 1 to 85 mg/l methanol and from 50 to 160 mg/l ammonia. The reduction of these two contaminants in the stripper bottoms was dependent on the percent overhead-to-feed ratios. For example, if 100 kg/min of process condensate was the feed rate to the steam stripper, then 10 kg/min of condensate overhead would represent a 10% overhead rate, and 5 kg/min of condensed overhead would represent a 5% overhead rate.

Test runs 19-28 were conducted with a portion of the overhead refluxed. This test did not give satisfactory results because a reflux pump did not function properly.

Test runs 29 and 31 were performed without reflux while runs 30 and 32 were with reflux. In these runs, ammonia in the stripper bottoms was reduced to very low limits (<5 mg/l). The percent overhead-to-feed ratios used to achieve these results was high (>10%). A typical 907 m. ton/day ammonia plant

generally produces about 45,400 kg/hr (757 l/min) of process condensate waste stream. If this 45,400 kg/hr is fed to a steam stripper, enough steam will be added to produce the desired overhead-to-feed ratio. For example, if a 10% overhead rate is needed for this separation, then enough steam is added to the column to vaporize the ammonia, methanol, carbon dioxide, and water to make up a total of 4540 kg/hr, which must be condensed prior to further in-house processing. The greater the overhead rate, the more steam is required, and the larger the vapor-liquid load to the column. Vapor-liquid loading to a column primarily controls the diameter sizing of a column. Therefore, if the overhead rate can be minimized, the economics for further handling of the overheads will be improved, especially in the case of reinjection of the stripped overheads into the primary reformer furnace process stream. The amount of overhead generated (for reinjection) from the stripper has a significant influence on the amount of energy required for condensation, pressurizing, re-evaporation, and injection of these overheads into the primary reformer furnace process. In order to decrease this overhead rate and still achieve the desired levels (<20 mg/l ammonia and methanol) in the stripped bottoms, the packing height and/or the refluxing rate has to be increased in the steam stripping column.

Process Effluent from Company 300

Test runs 33, 34, 36, 38, and 39 were without reflux, while runs 35 and 37 were with reflux. All runs were performed with the overhead rate less than 5% of the feed rate. The concentrations of the contaminants in the stripper bottom ranged from 10 to 35 mg/l for methanol and 25 to 53 mg/l for ammonia for test runs without reflux. The concentration of the contaminants in the stripper bottoms ranged from 1 to 7 mg/l for methanol and 29 to 39 mg/l for ammonia for test runs with reflux.

Process Effluent from Company 400

Test runs 40, 42, 44, and 46 were performed without reflux, and runs 41, 43, 45, and 47 were performed with reflux. The addition of reflux had a significant effect on the amount of methanol in the stripper bottoms. Methanol in the bottoms varied between 199 and 128 mg/l, and the ammonia between 73 and 145 mg/l for runs made without reflux. For runs with reflux, the methanol varied between 30 and 32 mg/l and the ammonia between 62 and 100 mg/l in the steam stripper effluent bottoms. With the addition of reflux, the reduction in concentrations averaged 25.7% for ammonia and 74.9% for methanol.

Process Condensate from Company 200

An effort was made in the final runs to perfect the stripping techniques for operating the pilot steam stripping column. Test runs 48, 49, 51, 53, 55, 57, 59, and 60 were performed without reflux, while runs 50, 52, 54, 56, 58, and 61 were performed with the addition of reflux. An effort was made to keep the reflux ratio at approximately 1:1. Residual methanol concentrations in the stripper bottom varied between 4 and 10 mg/l without reflux and between 1 and 53 mg/l with reflux. Residual ammonia concentration in the stripper bottom varied between 14 and 81 mg/l without reflux and 12 and 55 mg/l with reflux.

It was determined that from 5 to 6% overhead-to-feed rate was the optimum for the bench equipment and process conditions. Under these conditions, the methanol and ammonia concentrations in the stripper bottoms would be <15 mg/l and <20 mg/l, respectively.

Bench Steam Stripper Mass Balance

Mass balances were determined from the data collected during the operation of the bench steam stripper to validate the steam stripper data. These mass balances were determined for the methanol and ammonia content, as well as the volumetric throughputs. The volumetric balances were made by measuring the feed with a calibration peristaltic pump and comparing with an in-line rotameter. After cooling, the overhead bottoms were measured with a graduated cylinder. The deviation of the feed, with the sum of the overhead and bottoms, is shown in Table 15. Considering that flow rates varied from 10 to 250 ml/min, the overall volumetric balances for the runs evaluated were fairly consistent.

Vapor-Liquid Equilibrium Data

Prior to initiating the actual stripping runs on the bench unit, experimental vapor-liquid equilibrium measurements of ammonia in the process condensate were made. These data could be roughly correlated with the height of equivalent packing in the stripping column and would be needed in any subsequent design of a full-scale commercial steam stripping unit. Equilibrium data for the ammonia-water and methanol-water systems can be found in the literature. However, a literature search revealed no data for the quaternary system of ammonia-methanol-carbon dioxide-water.

TABLE 15. MASS BALANCES AROUND PILOT STEAM STRIPPER

Run No	Methanol % Error	Ammonia % Error	% Error By Volumetric	Run No.	Methanol % Error	Ammonia % Error	% Error By Volumetric
R-29	5.1	-15.7	-9.9	R-45	1.7	4.5	1.9
R-30	-3.8	-14.9	-14.8	R-46	8.2	8.4	7.2
R-31	1.5	54.6	-13.3	R-47	0.3	1.1	1.9
R-32	-15.7	21.2	-15.2	R-48	10.8	26.2	7.9
R-33	16.2	8.1	-4.4	R-49	6.4	-2.2	17.9
R-34	10.0	3.9	-5.1	R-50	13.9	11.2	4.7
R-35	8.2	5.0	-1.7	R-51	54.7	42.2	-6.9
R-36	25.3	3.3	-3.2	R-52	-9.1	-3.5	-8.0
R-37	-2.9	2.2	-1.0	R-53	-4.2	-6.6	-2.7
R-38	16.4	56.3	-2.7	R-54	-1.4	-4.9	-11.1
R-39	2.7	160.0	-2.8	R-55	16.0	4.6	2.0
R-40	15.7	-6.9	-2.2	R-56	11.5	-5.0	5.5
R-41	12.2	5.9	-1.1	R-57	2.4	13.8	-2.4
R-42	5.0	34.6	-4.6	R-58	6.6	17.2	-2.7
R-43	1.4	-5.5	-5.2	R-59	10.7	-11.2	-12.5
R-44	-21.2	1.1	-7.2	R-60	9.3	4.3	0.2
				R-61	4.5	7.4	2.3

Standard deviation was made on the data presented in Table 15. The formula used was as follows:

$$S^2 = \frac{n\sum x^2 - (\sum x)^2}{n(n-1)}$$

Vapor-liquid analyses were conducted on raw process condensate received from streams 200, 500, and 600. A diagram of the testing apparatus is presented in Figure 8. The following procedure was used to collect samples for analysis of the ammonia in the recovered vapor and liquid.

1. A total volume of 600 ml was initially charged to vessel A.
2. Ice bath water was circulated by pump B to condenser C to cold finger D and back to ice bath reservoir E.
3. Heater F was then turned on.
4. Valves 1, 2, and 4 were closed.
5. Valve 3 was opened and vented to atmosphere.
6. After still reached 100°C read by thermometer G, valve 3 was closed.
7. Approximately 20 min after systems reached equilibrium maintaining 100°C temperature, valve 1 was opened, and a 5 ml vapor sample was collected at H.
8. Syringe J was attached to needle I, valve 4 was opened, and approximately 15 ml was drawn off at the same time that the vapor sample was being collected.
9. After samples were collected, valves 1 and 4 were closed, and a 20-min period was designated between withdrawing samples.
10. Vapor and liquid samples were diluted and analyses for ammonia were made and recorded.

The first process effluent tested was from stream 200. The results are shown in Table 16. To check the variability of the runs, a least squares-fit of the data for the vapor (y) versus the liquid (x) equilibrium values was determined. The equation was as follows:

$$\text{Stream 200: } y = (147)(x) - 100$$

Where y = mole fraction of ammonia in vapor
x = mole fraction of ammonia in liquid

Subsequent runs on stream 500 and 600 produced the results shown in Table 17. The least-squares vapor-liquid equations for the two streams were as follows:

$$\text{Stream 500: } y = (123.5)(x) - 456$$

$$\text{Stream 600: } y = (232)(x) - 100$$

The vapor-liquid equilibrium data as represented by the preceding equations are plotted in Figure 9.

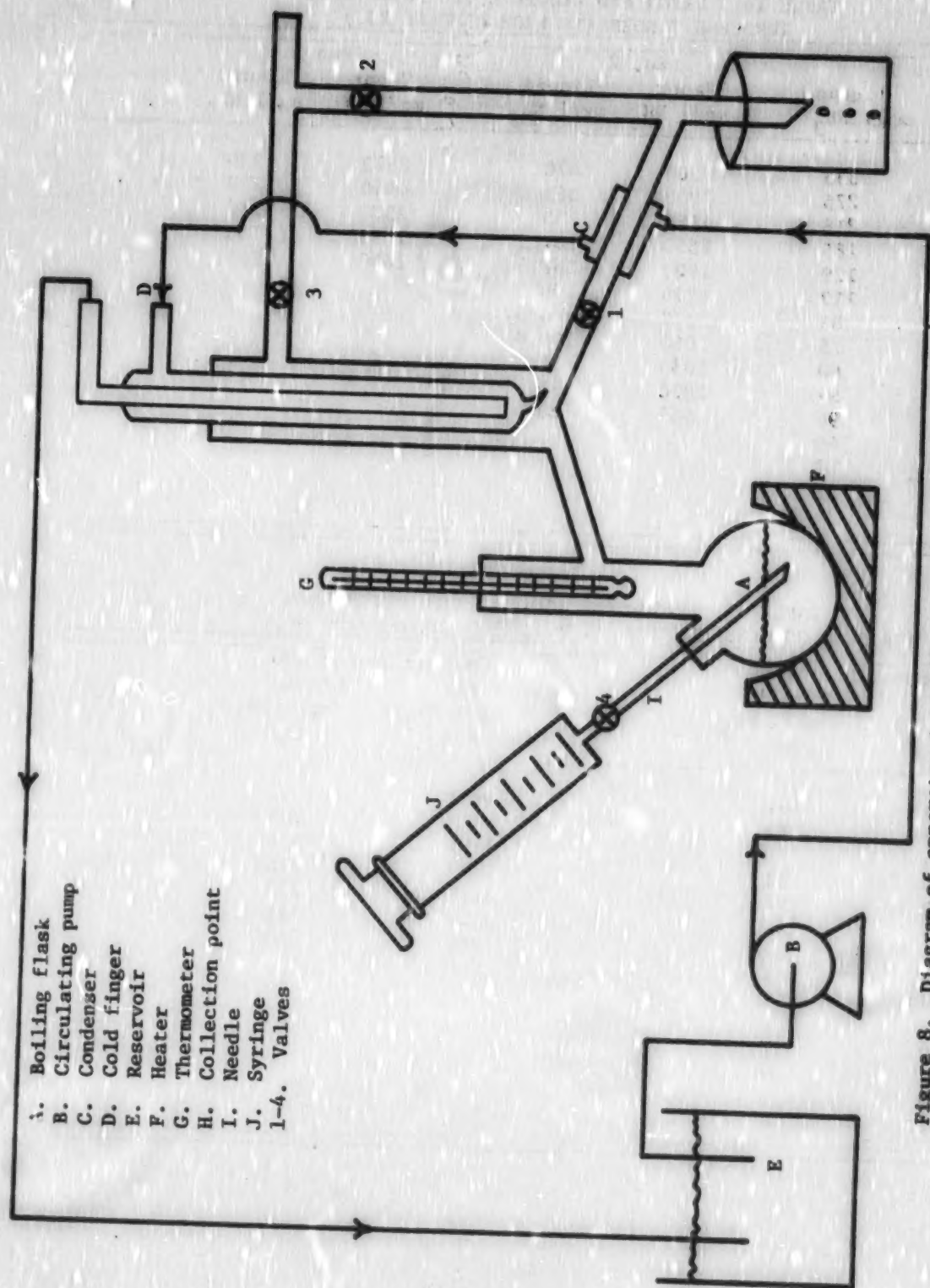


Figure 8. Diagram of apparatus to gather vapor-liquid data.

TABLE 16. VAPOR AND LIQUID EQUILIBRIUM DATA
(PROCESS CONDENSATE FROM COMPANY 200)

Run 1		Run 2		Run 3	
Vapor mg/l NH ₃	Liquid mg/l NH ₃	Vapor mg/l NH ₃	Liquid mg/l NH ₃	Vapor mg/l NH ₃	Liquid mg/l NH ₃
5400	335	8500	470	8875	330
2700	275	7700	363	4440	220
1820	218	4950	250	2500	180
1650	185	2550	187.5	1750	135
1100	129	1900	162.5	1650	135
930	113	1255	106.5		
725	83	870	78.5		
700	75	1060	100.0		
690	60	1030	84		
515	54	1050	95		
930	96	965	80		
475	45				
250	28				
220	27				
700	74				

TABLE 17. VAPOR AND LIQUID EQUILIBRIUM DATA
(PROCESS CONDENSATE FROM COMPANY 500 AND COMPANY 600)

Company Number 500		Company Number 600	
Vapor (mg/l NH ₃) (y)	Liquid (mg/l NH ₃) (x)	Vapor (mg/l NH ₃) (y)	Liquid (mg/l NH ₃) (x)
16440	144	24600	1140
12240	79	18720	708
11425	72	10080	336
7440	82	6600	276
5100	54	3840	222
3096	41	3120	171
2495	24	1980	150
1850	17		
684	11		
456	8		
380	7		
240	6		
228	5		
148	4		

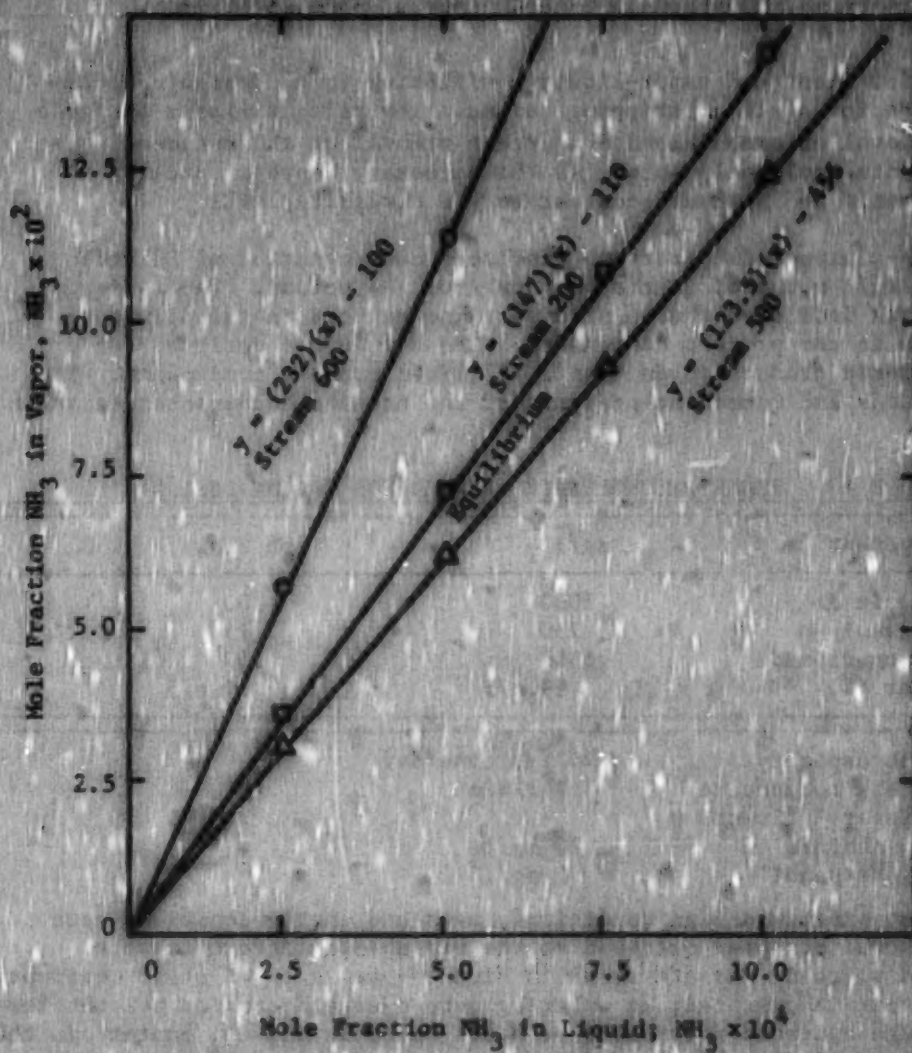


Figure 9. Equilibrium curve for ammonia/methanol wastewater system.

SECTION 7

DESIGN OF COMMERCIAL AMMONIA-METHANOL STEAM STRIPPER

Using pilot plant and vapor-liquid equilibrium data, design calculations were made for a steam stripping column. The pilot stripper achieved 98 percent removal of ammonia and 99 percent removal of the methanol. The vapor-liquid data would help establish the necessary depth of packing to reduce the ammonia and methanol content to the specified level.

The bench-stripper data corresponded to a concentration of 30 mg/l ammonia and 5 mg/l methanol in the bottoms from the column. Vapor-liquid equilibrium data indicated that a straight line existed in the dilute ammonia concentrations in the process condensate. The column was designed for a 907 m. ton/day ammonia production unit with 757 l/min process condensate. The design conditions and component analysis of the process condensate are shown in Table 18.

TABLE 18. PROCESS CONDENSATE ASSUMED FOR COLUMN DESIGN

Component	mg/l	pph flow
Ammonia	1000	100
Methanol	750	75
Carbon dioxide	1500	150
Water (X)	99.675	99.675

Plant capacity	907 m. tons/day
Process condensate	757 l/min
Stripper Effluent	
Ammonia	20 mg/l
Methanol	5 mg/l

To develop optimum design conditions, mass and energy equations were developed with the stripper overhead as the variable. These data were correlated and plotted, and are shown in Figure 9 as kg/hr of steam consumption vs. water content in overhead; kg water/kg pure overhead; and/or percent feed as overhead. (Pure overhead = combined methanol, ammonia and CO₂ content in the overhead.) Theoretical process conditions used to develop the design were as follows:

1. 45,400 kg/hr feed rate to the steam stripper with the composition as shown in Table 16.
2. Low pressure steam (3.16 kg/cm² gauge).
3. Vapor density (0.769 g/l).
4. Liquid density (0.862 g/cm³).

5. Liquid viscosity (0.29 centipoise).
6. 3.8 cm (1.5 inch) Pall rings for packing material with a factor of 3.9.
7. Feed preheated prior to stripper column entry.
8. 98 percent removal of ammonia and 99 percent removal of methanol and carbon dioxide.

With the above conditions, approximately 150 kg/hr total of ammonia, methanol, and carbon dioxide are fed into the steam stripper along with the process wastewater. If there were an infinitely large column, it would be possible to use only enough steam to bring the column and its contents up to temperature for removal of the contaminant. In this case, there would be 145.5 kg/hr of pure overhead (44.5 kg/hr of ammonia, 33.7 kg/hr of methanol, and 67.3 kg/hr of carbon dioxide), without any water carryover into the overhead. At this time, such an operation is not economically feasible. However, if enough water was taken with this 145.5 kg/hr of contaminant, calculations could be made to determine how much steam would have to be added to the stripper. For example, on the abscissa (Fig. 10), 1 kg water/kg pure overhead would represent a 50% water and 50% ammonia, methanol, and carbon dioxide. If the 50% ammonia, methanol, and carbon dioxide represents 145.5 kg/hr, then the 50% water represents 145.5 kg/hr. Therefore, 145.5 kg/hr of water divided by 145.5 kg/hr of pure overhead represents the 1 kg/hr in the abscissa. The 10 kg/hr would represent 1455 kg/hr of water and 145.5 kg/hr of ammonia, methanol, and carbon dioxide. Also shown on the abscissa is a scale showing the percent feed as overhead. For example, the 1 kg of water/kg pure overhead represents 145.5 kg/hr of water and 145.5 kg/hr of ammonia, methanol, and carbon dioxide, for a total of 291.0 kg/hr of overhead. If the feed rate is 45,400 kg/hr, there will be 0.6% feed in the overhead (291.0 kg/hr divided by 45,400 kg/hr multiplied by 100). The 10 kg of water/kg of pure overhead has a total of 1455 kg/hr of water with 145.5 kg/hr of ammonia, methanol, and carbon dioxide, representing a total overhead of 1600.5 kg/hr. In this case, there will be 3.53% feed as overhead. The concentration in the overhead can be determined using the data in Figure 10.

Figure 11 is a plot of the tower diameter vs. pressure drop for steam rates from 454 to 9072 kg/hr. With this plot, the required column diameter for the separation can be determined where the pressure drop and steam rate are known.

The water content of the stripper overhead was minimized to reduce the total volume for further handling. If an ammonia concentration of 6 percent in the overhead could be achieved, the total overhead volume would be reduced to some 19-38 l/min. The design was based on packed tower concepts. The basic equation for packed tower design was:

$$\Delta P = a(10^{bL}) \left(\frac{G^2}{P_s} \right)$$

where ΔP = Pressure drop

a, b = Constants for a particular packing

G = Vapor mass velocity

L = Liquid mass velocity

P_s = Vapor density

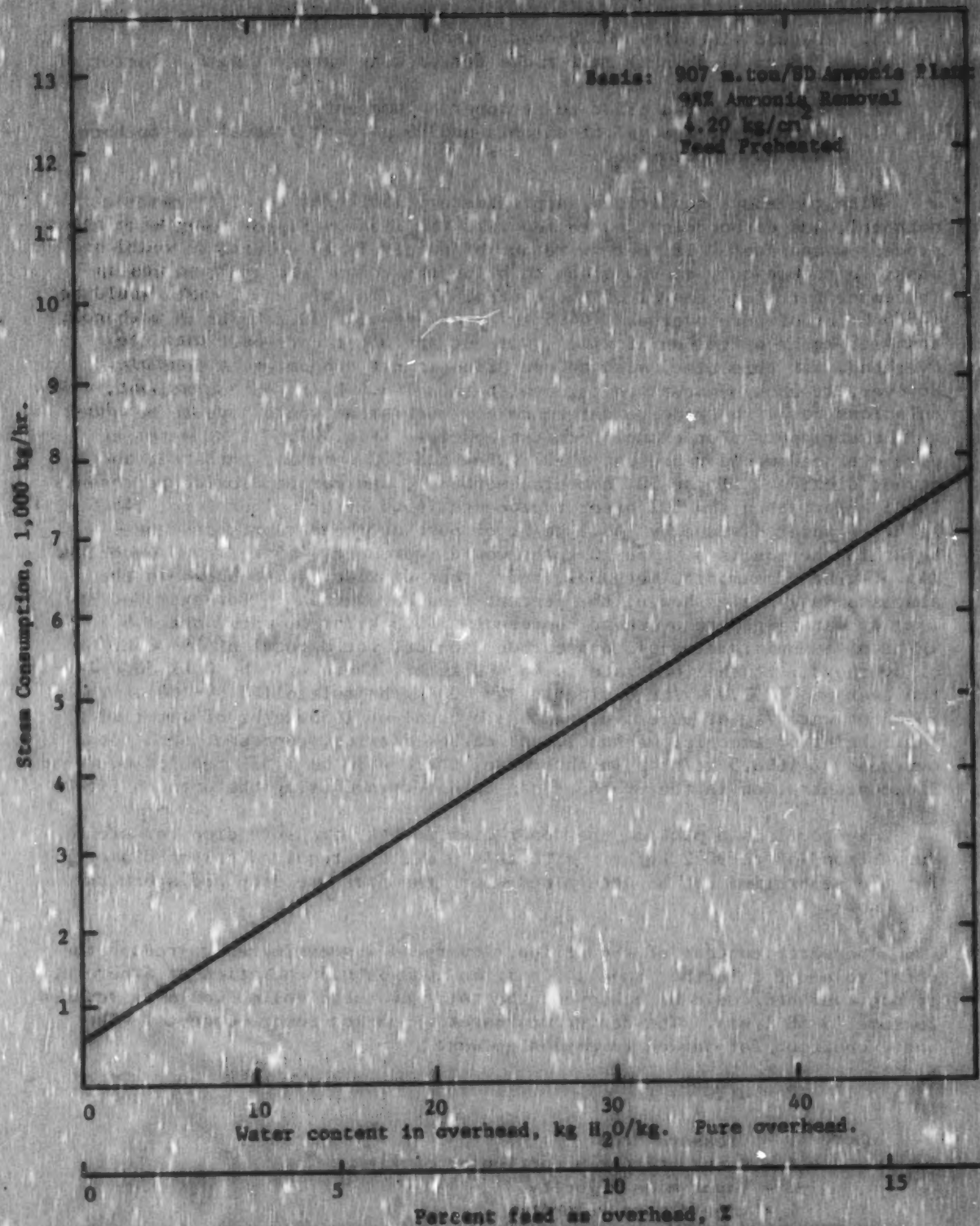


Figure 10. Steam consumption vs. water content in overhead and percent feed taken as overhead.

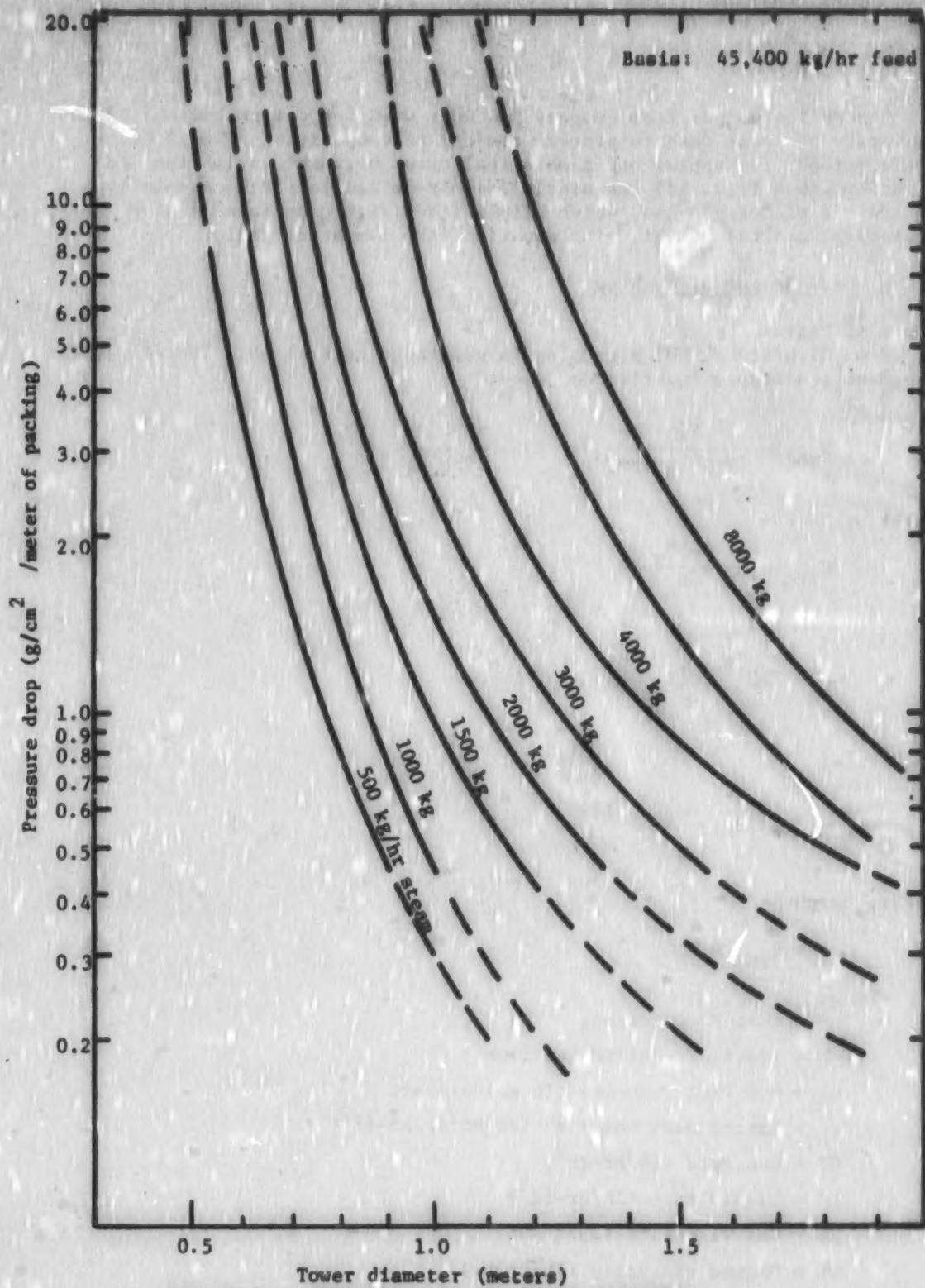


Figure 11. Pressure drop vs. tower diameter.

Vapor-liquid data from company 500 were used for design because of the similarity of these data to process condensate composition. The McCabe-Thiele method of stepping off theoretical trays between equilibrium and operating lines (Fig. 12) was used. Another method to check calculations was the use of Henry's law, which simplifies design equations to give theoretical packing height. The equations are summarized below.

To Calculate Height of Packing

Number of Units--

From literature, NH_3 stripping is gas-phase controlled. Therefore, the gas-phase resistance equation was used:

$$N_{\text{TOG}} = \frac{y_B - y_T}{(y-y^*)_B - (y-y^*)_T} \ln \frac{(y-y^*)_B}{(y-y^*)_T}$$

Height of Unit--

$$H_{\text{TOG}} = H_G + \frac{MG}{L_m} (H_L)$$

Where:

$$H_G = \frac{\alpha G'^B}{L' \alpha} \frac{1}{P_G D_G}^{1/2}$$

$$H_L = \phi \left(\frac{L'}{\mu L} \right)^J \frac{1}{P_L D_L}^{1/2}$$

Packing Height--

$$Z = H_{\text{TOG}} N_{\text{TOG}}$$

Where:

y = Mole fraction NH_3

M = Slope of equilibrium line

G_m = Gas mass velocity (lb moles/hr-ft²)

L_m = Liquid mass velocity (lb moles/hr-ft²)

G' = Gas rate (lb/hr-ft²)

L' = Liquid rate (lb/hr-ft²)

μG = Gas viscosity (lb/ft-hr)

μL = Liquid viscosity (lb/ft-hr)

P_G = Gas density (lb/ft³)

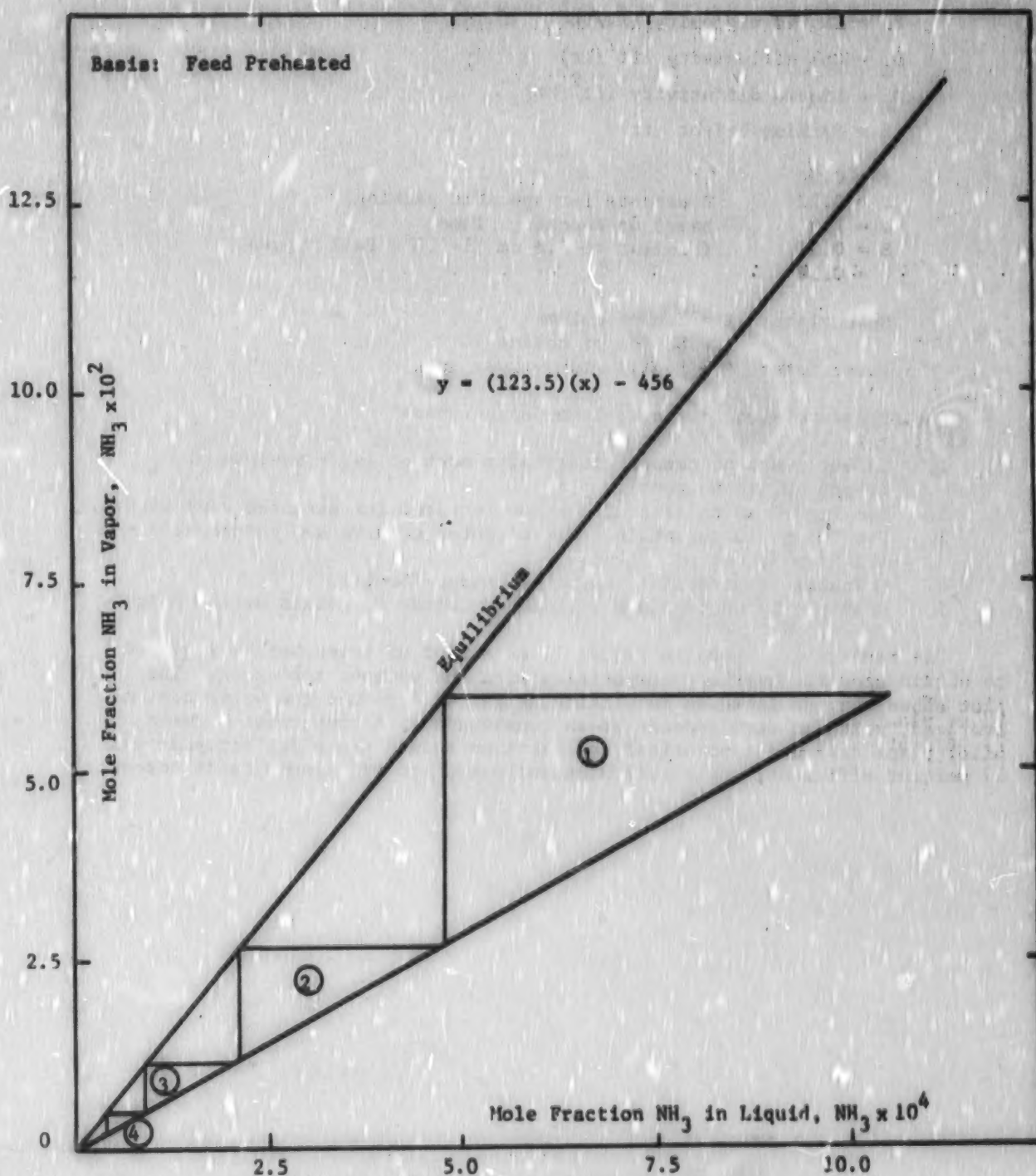


Figure 12. McCabe-Thiele method for theoretical stages.

μ_L = Liquid viscosity (lb/ft³)
 D_G = Gas diffusivity (ft²/hr)
 D_L = Liquid diffusivity (ft²/hr)
 Z = Packing height (ft)

ϕ = 0.01
 J = 0.22 Constants for specific packing;
 α = 7.0 based on Rasching rings
 B = 0.39 (similar to 3.8 cm [1-1/2"] Pall rings)
 γ = 0.58

Subscripts: T = Top of column
 B = Bottom of column

Superscripts: * = Equilibrium value.

The procedure used for the column design was:

1. Select overhead composition; water content (with maximum of 20 ppm NH₃ in bottoms).
2. Use Figure 10 to determine steam required for overhead composition.
3. Use Figure 10 to obtain tower diameter to give a pressure drop = 4.2 g/cm²/meter of packing.
4. Calculate theoretical height by McCabe-Thiele.
5. Multiply by appropriate efficiency factor to obtain actual height.

The results are shown in Figure 12 as a plot of tower height required to obtain specific overhead composition with and without refluxing. The plot shows that an increase in packing height will reduce the water content overhead, which in turn reduces steam consumption. A comparison between pilot plant data and theoretical calculations showed the pilot stripper was 27 percent efficient, while refluxing increased the efficiency to 36 percent.

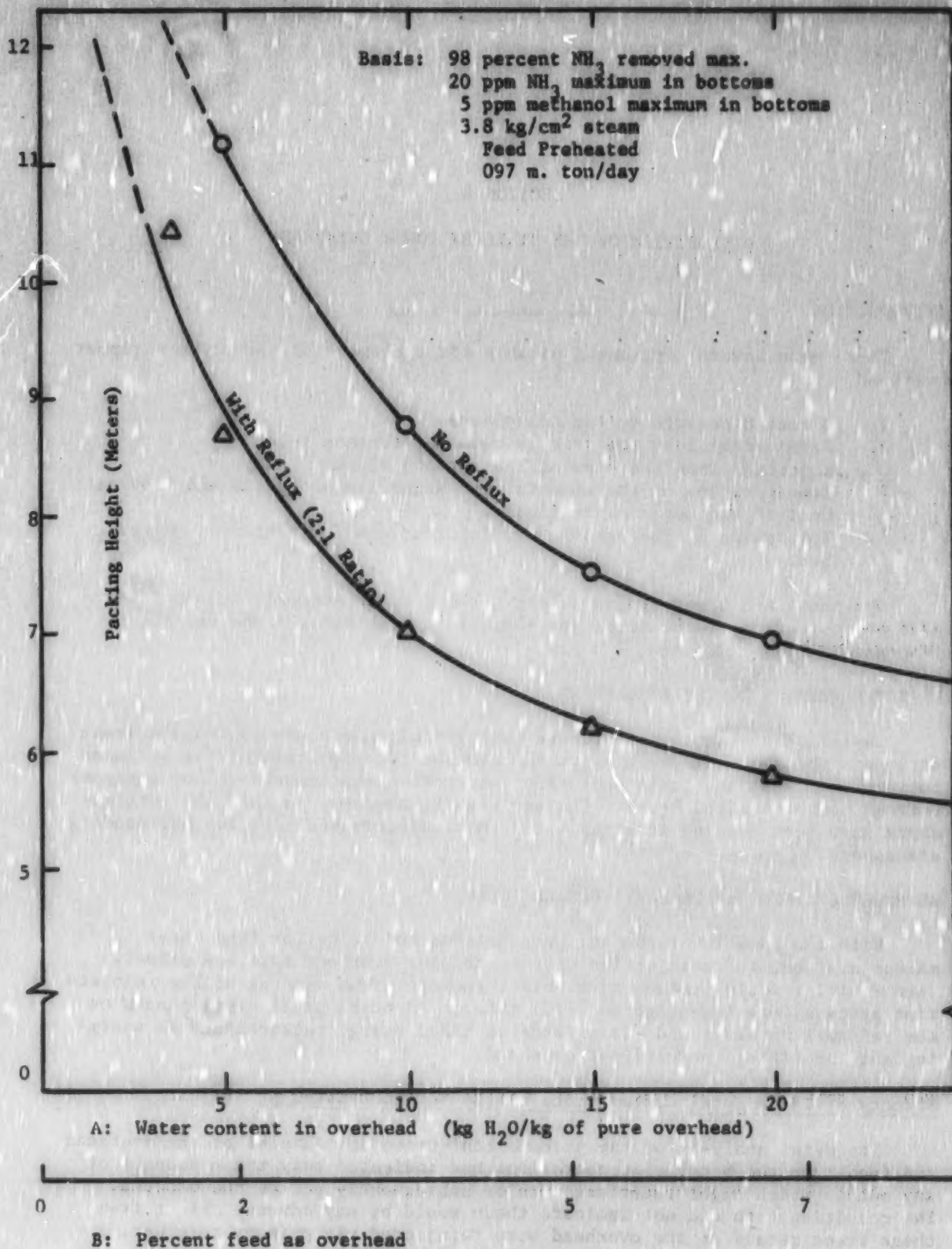


Figure 13. Commercial column design.
Packing height vs. overhead water content.

SECTION 8

DISPOSITION OF THE STRIPPER TOWER OVERHEAD

INTRODUCTION

There were several options available for treatment of the steam stripper overhead.

1. Direct discharge to the atmosphere.
2. Reinjection into the primary reformer furnace inlet.
3. Injection into the base of the furnace stack.
4. Precipitation of the ammonia with magnesium phosphate and biotreatment of the methanol residuals.
5. Adsorption of the ammonia utilizing a vanadium pentoxide packed bed.

Options 4 and 5 were to be investigated from an economic standpoint to give an indication of the total cost-benefit comparisons of the various processes (see Section 10).

DIRECT DISCHARGE TO THE ATMOSPHERE

Several large ammonia producers have installed process condensate steam strippers which are discharging to the atmosphere. Analysis of the stripper bottoms indicates that this operation does reduce the ammonia in the stripper bottoms to the desired level. The net result, however, is that the contaminants have been removed from the water and redistributed into the surrounding atmosphere.

REINJECTION INTO THE PRIMARY FURNACE INLET

With the recycle of the stripper bottoms to the boiler feed water makeup station, the reinjection of the stripper overhead into the primary furnace inlet would produce total plant recycle. Two aspects of the reinjection process were investigated: (1) effects of trace metal contaminants on the reformer catalyst and (2) effects of added energy requirements in sparging and vaporizing the stripper overhead.

Effects of Trace Metal Contaminants on the Reformer Catalyst

The metal analysis of the process condensate and samples of the overhead and feed from the bench unit operations had indicated only trace amounts of any metals which might interfere with or subsequently poison the process. The resulting data did not indicate there would be any adverse effect from these trace metals if the overhead were reinjected via primary reformer.

Effects of Added Energy Requirements in Sparging and Vaporising the Stripper Overhead

The primary reformer feed is a proportioned mixture of steam and natural gas at approximately 38 kg/cm^2 and 315°C . It is preheated to this temperature prior to the furnace inlet. The stripper overhead would have to be pressured for injection at these conditions. A schematic of the flow conditions is shown in Figure 14.

Since there is no preheat source, the heat of vaporization and sensible heat required to bring it up to process conditions would have to come from the steam and methane. The net result is an overall reduction in the temperature of the feed to the primary furnace. The temperature of the primary reforming operation is critical to the conversion of the methane and steam to carbon monoxide and hydrogen. If the temperature of the furnace inlet is decreased, the only way of achieving the desired conversion temperature is to decrease the quantity of feed to the furnace, which results in an overall reduction in plant production capacity. Energy and mass balance calculations were performed around the point of reinjection to determine the net decrease in the primary furnace inlet temperature due to the sparged stripper overhead. Three different process temperature conditions, 49°C , 60°C , and 121°C , were tried for the condensed stripper.

To determine the effect of the amount of stripper overhead on the production capacity, material and energy balances were determined on the reinjection of varying amounts the overhead. The following basis was assumed for these calculations.

907 m. ton/day ammonia plant
45,400 kg/hr of process condensate
Process condensate contaminants
 NH_3 1,000 mg/l
 Methanol 750 mg/l
 CO_2 1,500 mg/l
Primary furnace inlet at 38 kg/cm^2 and 315°C
Stripper overhead at 49°C , 60°C and 121°C .

A plot of the inlet conditions of the primary reformer versus varying amounts of stripper overhead is shown in Figure 16.

For the design conditions initially specified, the net decrease in the primary reformer inlet temperature would be 21°C if a 6.73% overhead rate from the steam stripper was injected into the process at the point shown in Figure 14. This 6.73% overhead rate corresponds to a water content of 20 kg/hr of pure overhead (2909 kg/hr of water and 145.5 kg/hr of ammonia, methanol, and carbon dioxide, for a total of 3054.5 kg/hr of condensed overhead). Thus, the amount of water present in the stripper overhead is critical to the amount of reduced temperature for the ammonia production.

Figure 15 was prepared to determine the amount of extra heat which would have to be added for varying amounts of stripper overhead injected into the furnace inlet. This plot represents the percent increase in furnace

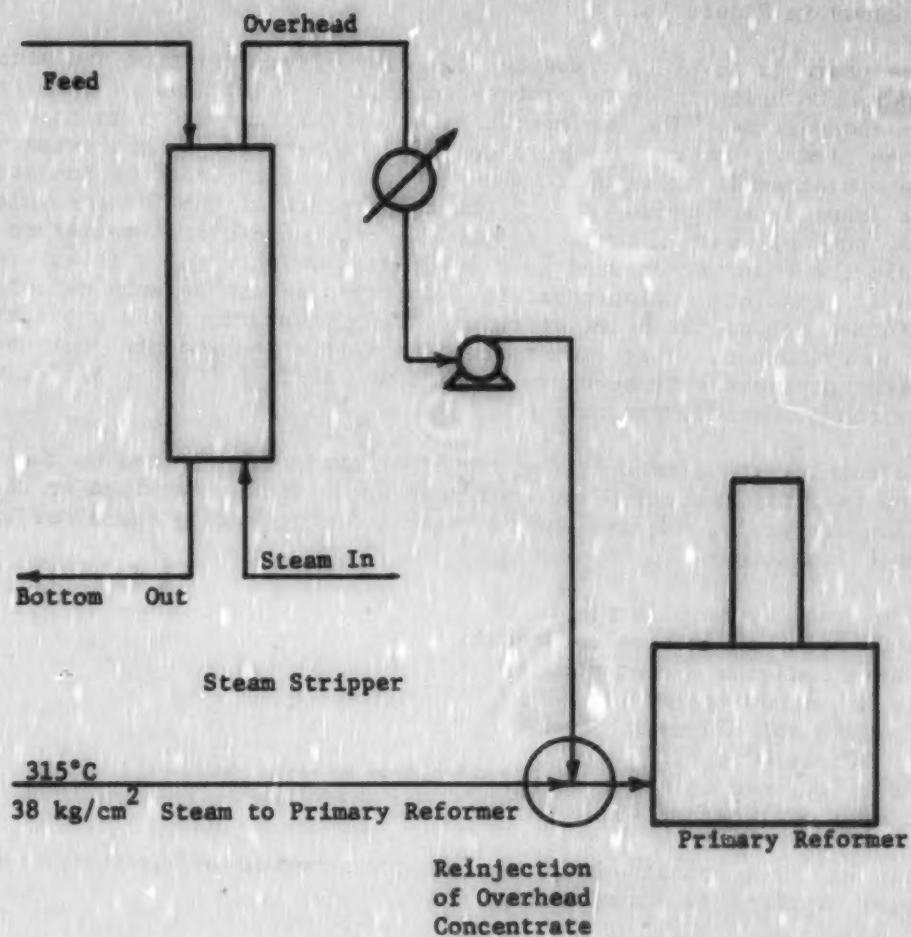


Figure 14. Stripper overhead to primary reformer.

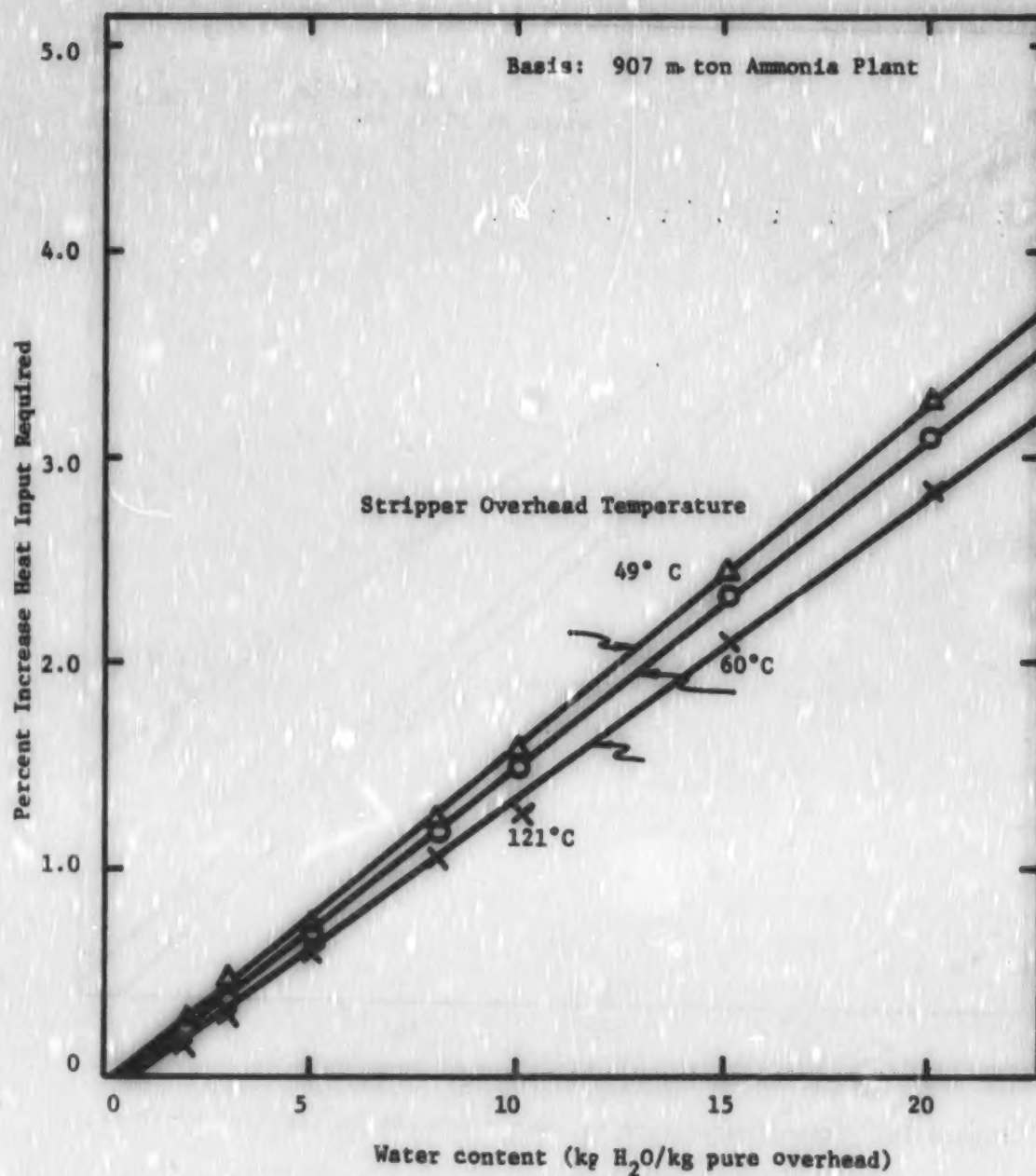


Figure 15. Percent increase in heat required to maintain reformer temperature vs. water content in stripper overhead.

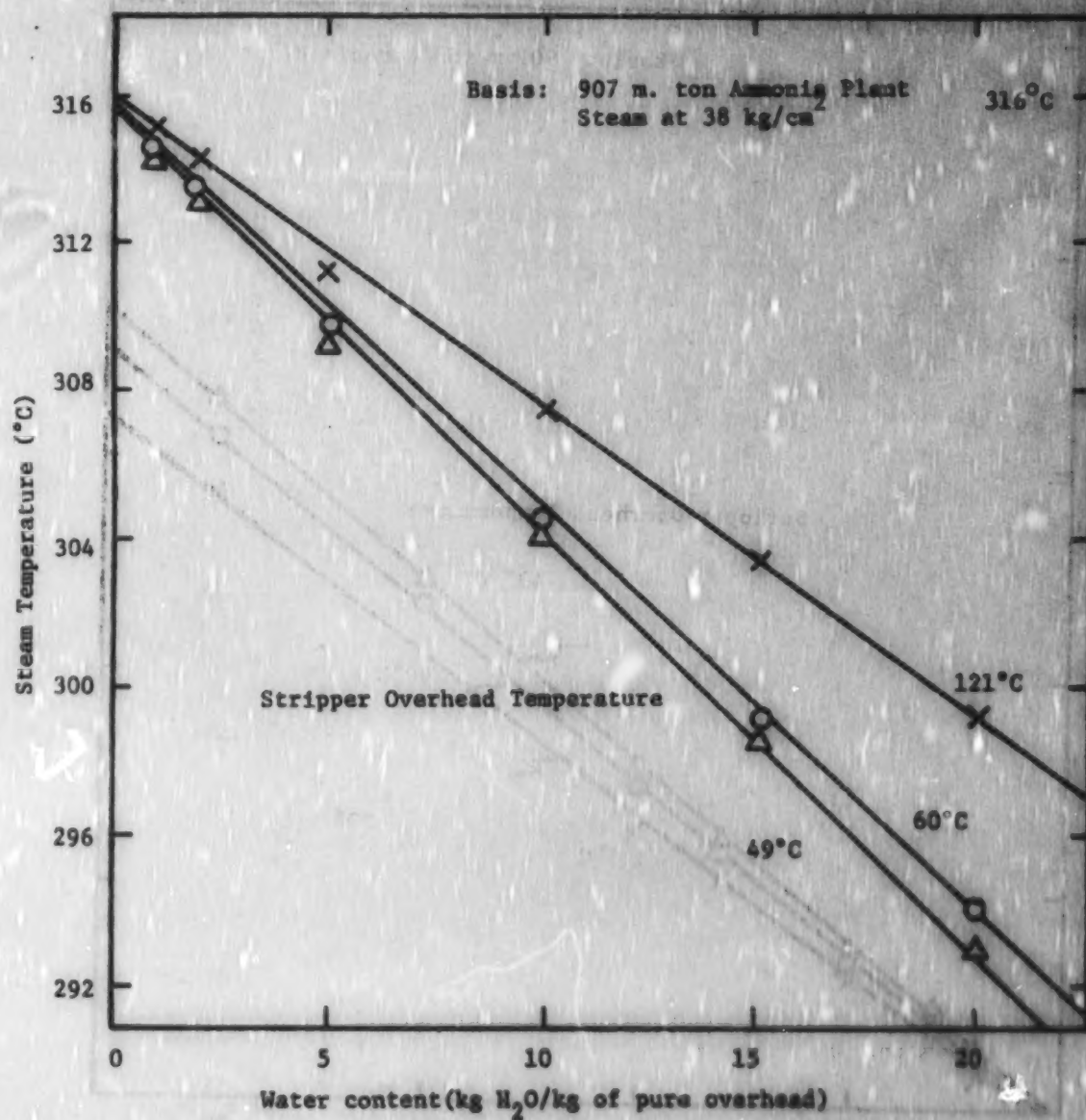


Figure 16. Steam temperature vs. water content in stripper overhead.

heat needed to maintain an exit temperature of 825°C and 30 kg/cm^2 in the primary reformer. Again, three different temperatures were used for the process condensate, and various amounts of water were included in the stripper overhead. For example, the $20\text{ kg H}_2\text{O/kg}$ of overhead is approximately 95% H_2O ; at 60°C , a 3.1% increase in heat input is necessary to maintain the same conditions prior to injection of the steam stripper condensate.

Approximately 440 m^3 of natural gas per m. ton of ammonia is required as the heating fuel in the primary furnace. If a 3.1 percent increase in heat is necessary, an additional $12,300\text{ m}^3/\text{day}$ of natural gas would be needed to maintain production capacity.

Minimum Stripper Overhead to Achieve Satisfactory Bottoms Concentrations of Contaminants

If the removal of the ammonia and methanol contaminant vapor could be accomplished with minimum stripping, the quantity of stripper overhead condensate would be reduced considerably. The impact of reduced water reinjection into the furnace inlet would be reflected in a smaller reduction in the temperature. For example, if the overhead from the stripper were reduced to $5\text{ kg H}_2\text{O/kg}$ of pure overhead components (1.92% of feed taken overhead), the percent extra heat input to the primary furnace would drop from 3.1 percent to 0.5 percent. Under these conditions, a 907 m. ton/day ammonia plant would require heat input of $14,300\text{ m}^3/\text{day}$ rather than $12,300\text{ m}^3/\text{day}$.

To reduce the stripper overhead from 6.73 percent to 1.92 percent of the feed would require that the stripper be almost doubled in height. This added height would at least double the cost of the stripper installation. Further, any additional heat input would require the installation of another furnace to add the lost heat to the process system.

Additional Equipment for Stripper Overhead Reinjection

Equipment purchases in addition to the steam stripping unit required for primary furnace reinjection would include:

Overhead Condenser Unit—

Based on the 2268 kg/hr , the heat load would be $1,329,000\text{ Kcal/hr}$, utilizing approximately 16 m^2 of condenser surface with a throughput of 1100 l/min cooling water. If a reflux of 2:1 were used, the surface area would be increased to 59 m^2 with approximately $3,906,000\text{ Kcal/hr}$ heat load utilizing over 3,400 l/min of cooling water.

Feed Pump—

A high pressure, low capacity feed pump is needed. This pump has to deliver from 4 to 40 l/min at 30 kg/cm^2 to the sparger.

Auxiliary Tubular Furnace—

This furnace would preheat the stripper overhead to the process conditions existing at the furnace inlet. Based on 6.73 percent overhead, the furnace duty would be $6,300,000\text{ Kcal/hr}$ with an efficiency of 75 percent.

INJECTION OF STRIPPER OVERHEAD VAPOR INTO THE FURNACE STACK

Theoretical Decompositions

Injection of the stripper overhead vapor containing ammonia and methanol offered an interesting possibility. At the stack temperature of 200°C to 260°C, ammonia and methanol would largely decompose. In order to evaluate this method of disposal, the thermodynamic equilibrium of ammonia and methanol in the presence of stack exhaust gases was calculated for the 200°C to 260°C temperature range.

To calculate the free energy of decomposition, the products of decomposition from the ammonia and methanol were defined as shown in the following equations:

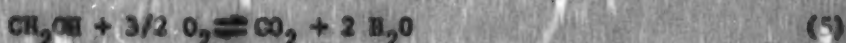
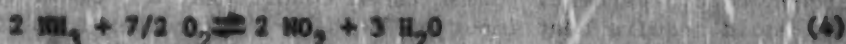
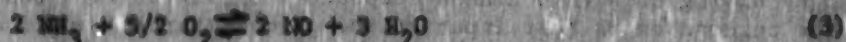


Table 19 presents the free energy of the assumed reactions as a function of temperature. Using the data developed in this table, it was possible to plot the free energy for the assumed decomposition equations as a function of temperature. This plot would indicate the potential decomposition to those products which might be expected in the furnace stack. This plot is shown in Figure 17. If oxygen was not present in the stack, 90 percent of the ammonia would decompose to nitrogen and hydrogen at a temperature of approximately 254°C. Also at this temperature, 99 percent of the methanol would decompose into carbon monoxide and hydrogen. If oxygen was present, then the decomposition of the ammonia would be through the mechanism of equations (3) and (4). In general, furnace stack gases contain very little excess air, as this condition is not in the interest of maximum heat utilization of available fuel.

PRECIPITATION OF THE AMMONIA WITH MAGNESIUM PHOSPHATE AND BIOTREATMENT OF THE METHANOL CONTAMINATED WASH WATER

No experimental data was determined for this process technique. However, a cost-benefit evaluation based on assumed operating conditions was developed. Data for this process were furnished by Dr. R. Swank of the Environmental Protection Agency. The cost-benefit evaluation appears in Section 10.

TABLE 19. GIBB'S FREE ENERGY CALCULATIONS

Reaction	Temperature (°C)	Free Energy cal/g mole
$\text{CH}_3\text{OH} + \text{CO} + 2\text{H}_2$	149	-635.4
	197	-1058.3
	177	-2161.2
	204	-4121.7
	232	-5166
	260	-6724
$\text{NH}_3 + 1/2\text{N}_2 + 3/2\text{H}_2$	149	925.5
	177	218.3
	204	-506.9
	246	-1567.2
	254	-1802.9
$2\text{NH}_3 + 5/2\text{O}_2 + 2\text{NO} + 3\text{H}_2\text{O}$	149	-91,849
	204	-97,825
	260	-93,712
$2\text{NH}_3 + 7/2\text{O}_2 + 2\text{NO}_2 + 3\text{H}_2\text{O}$	149	-101,465
	204	-100,837
	260	-100,804.8
$\text{CH}_3\text{OH} + 3/2\text{O}_2 + \text{CO}_2 + 2\text{H}_2\text{O}$	149	-130,014
	204	-120,340
	260	-131,074.9

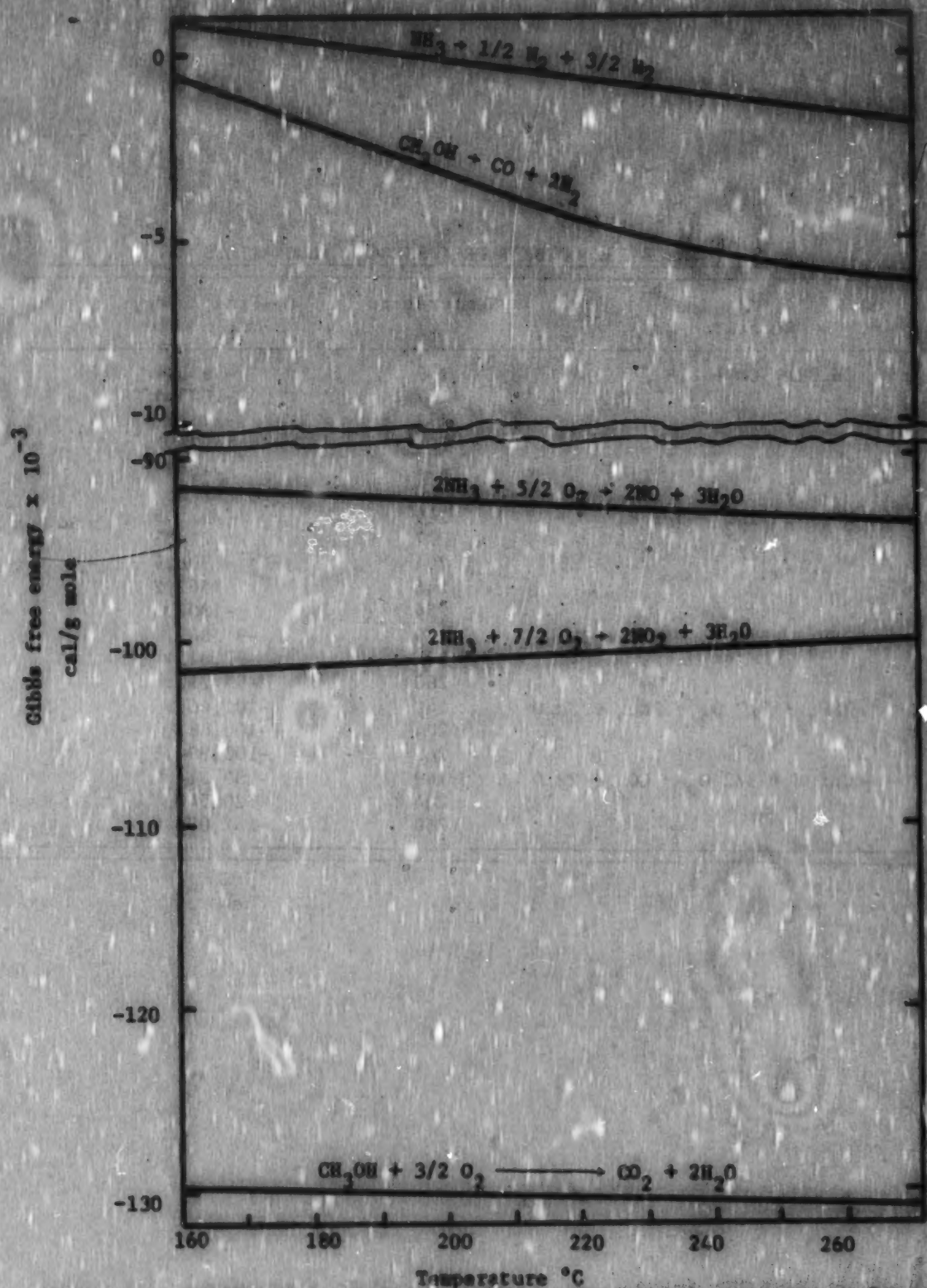


Figure 17. Gibbs' free energy for ammonia and methanol reactions at furnace stack temperatures.

SECTION 9

EVALUATION OF COMMERCIAL STEAM STRIPPER WITH OVERHEAD INJECTION INTO THE FURNACE STACK

INTRODUCTION

The theoretical thermodynamic analysis of the decomposition of the ammonia and methanol within the furnace stack offered an attractive, economical solution to the disposal of the stripper overhead. The stripper bottoms could be recycled to the boiler feedwater systems. During this program, one of the ammonia plants installed a stripper which diverted the overhead into the primary furnace stack. To corroborate the data obtained earlier with the bench unit and the thermodynamic equilibrium calculations, field tests were conducted on this commercial unit.

COMMERCIAL STRIPPER PROCESSING CONDITIONS

The commercial column was designed with a 9.1 m stripping section and packed with Pall rings. The overhead stripping line entered the furnace stack approximately 8 m from the ground. The stack stood 32 m high. A schematic of the stripping towers, overhead vapor line, and furnace stack is shown in Figure 18.

Since the intent of the field test work was to determine the amount of ammonia and methanol decomposed in the stack, sample points were installed to measure flow and obtain representative samples. These points are indicated in Figure 18. Sampling of the furnace stack below and above the stripper vapor entrance gave an indication of the components added to the furnace exhaust gases. Measurement of the vapor from the stripper overhead would permit determination of the amount of stripper components being decomposed.

Sampling Steam Stripper

A number of test runs were made on the steam stripper to obtain reliable operating data. Because the overhead was vapor, a cooler had to be installed to condense and sub-cool this condensate to insure total recovery. A diagram of the feed test equipment is shown in Figure 19.

Sampling Stack Analysis

The furnace stack was sampled at two points: (1) at the furnace outlet and (2) above the stripper overhead injection point. With this sampling

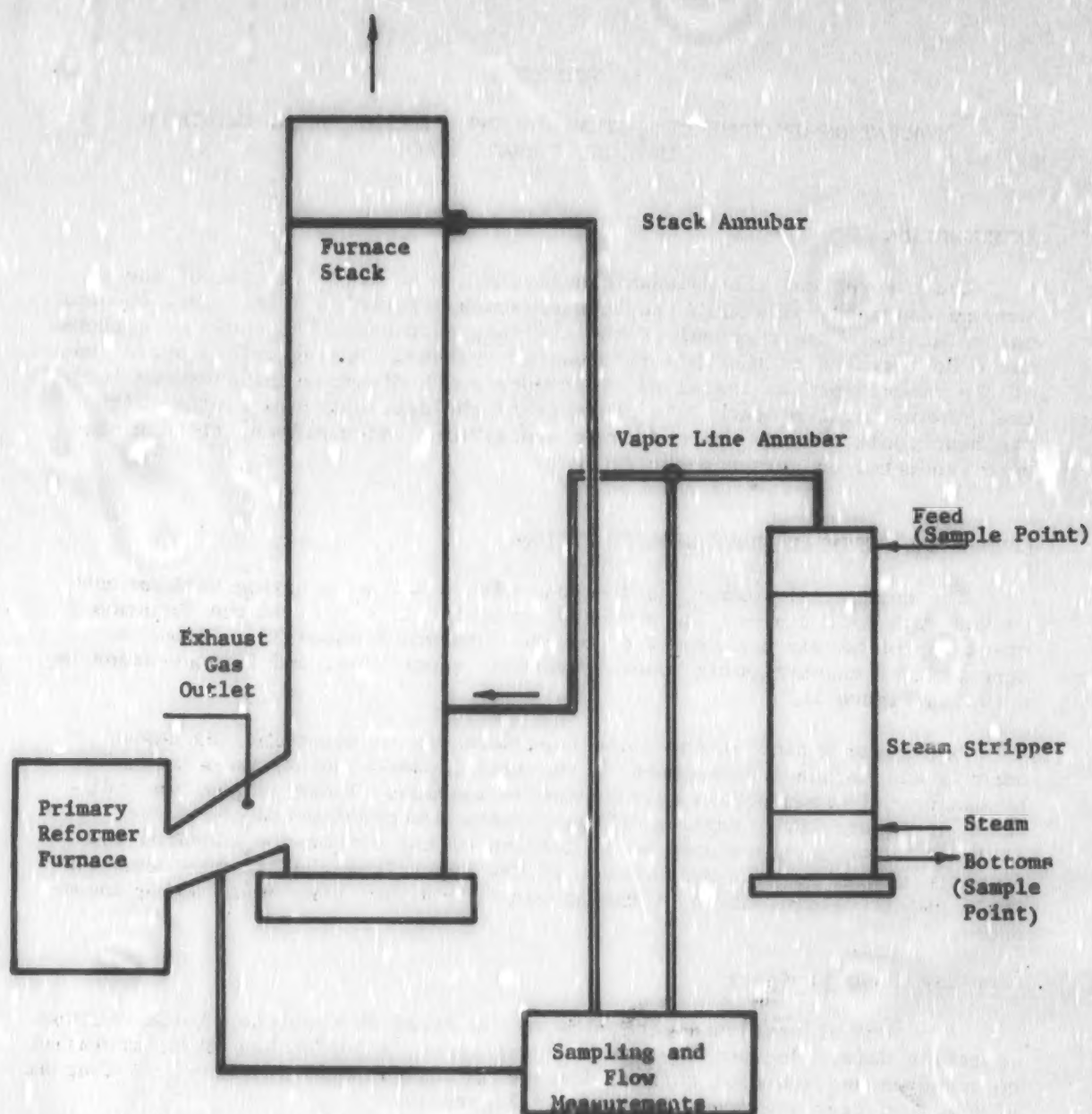


Figure 18. Plant schematic showing location of five sample points for test runs.

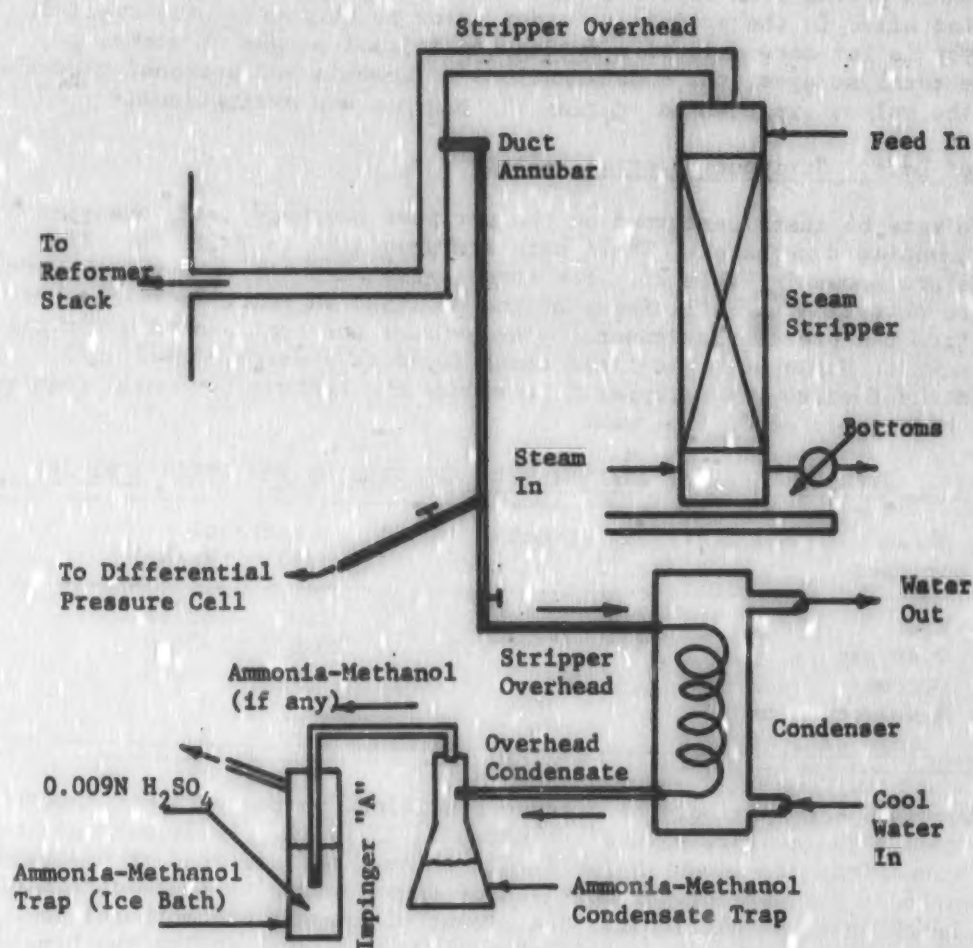


Figure 19. Ammonia/methanol sample train for stripper overhead analysis.

procedure, the status of the ammonia and methanol constituents could be accurately determined. The sampling train used for this analysis is shown in Figure 19.

Data Collection

A total of 74 runs were made on the steam stripper (runs 1-9 were no data-familiarization runs); determinations were made of the flow conditions and the individual component analysis. Also, appropriate measurements were taken at the two sampling points in the stack during these stripper tests. These data are presented in Tables 21 and 22. The measurements were made over a 3-month period from September 1976 to January 1977. A new catalyst had been installed in the primary reformer prior to this evaluation period. The catalyst is far more selective during the initial stages of operation, and as the catalyst ages, the concentrations of ammonia and methanol gradually approach the values experienced during the bench-scale evaluations.

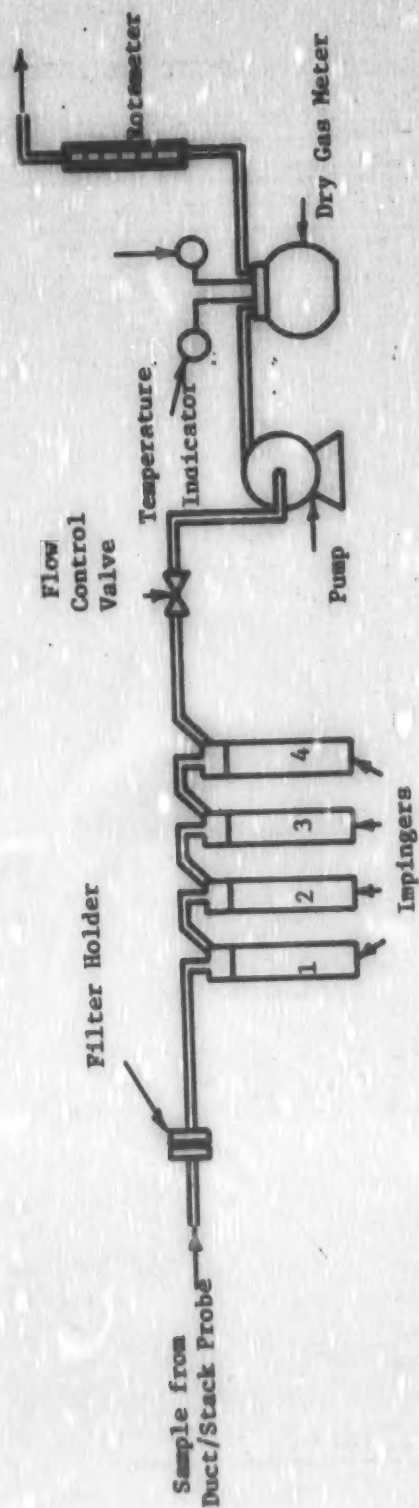
Analysis of Data: Stripper Material Balance

There were 65 tests performed on the stripper overhead, with analyses made for ammonia and methanol. These data are presented in Table 21. Flow conditions are shown in Table 22. For comparative purposes, the values were averaged to determine the efficiency of the stripper in removing ammonia and methanol from the process condensate. The average chemical analysis for all runs is shown in Table 20. The field tests found an average of 487 mg/l ammonia in the feed to the stripper. To reduce the bottoms to 7 mg/l required a removal efficiency of 96.8 percent.

TABLE 20. AVERAGE CHEMICAL ANALYSIS FOR ALL RUNS ON THE STEAM STRIPPER

Steam Stripper	Ammonia		Methanol	
	(mg/l)	(kg/hr)	(mg/l)	(kg/hr)
Feed	487	39.2	262	21.1
Overhead	4750	37.9	2610	20.8
Bottom	7	1.3	3.4	0.3
% Reduction of both products		96.8		98.8

During this same period, the process conditions on the stripper towers were recorded. The average values are shown in Table 22. Daily averages of the flow conditions are shown in Table 20. These data indicated an overhead-to-feed ratio of 9.9 percent. Comparison of these data with those obtained from the bench unit was difficult. The amount of ammonia and methanol in the process condensate was about half that which was found during the bench scale test work.



Impinger 1 - 100 ml 0.009N H_2SO_4

Impinger 2 - 100 ml 0.009N H_2SO_4

Impinger 3 - Dry

Impinger 4 - Anhydrous $CaSO_4$ (Drierite)

Figure 20. Ammonia/methanol sampling train for stack analysis.

TABLE 22. FIELD DATA

Material Flow around Combustion										Discharge from Reference Stack									
Steam Stripper										Total									
Run	Feed	Steam	Overhead	Bottom	Overhead	Bottom	Feed	Steam	Overhead	Bottom	Feed	Steam	Overhead	Bottom	Feed	Steam	Overhead	Bottom	Feed
kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr	kg/hr
50	83,279	8,981	8,255	84,005	9,752	403,007	—	—	—	—	—	—	—	—	—	—	—	—	—
51	79,817	8,709	8,119	80,527	9,457	390,827	16.9	43.3	6.1	15.6	—	—	—	—	—	—	—	—	—
52	77,092	8,537	7,902	77,727	9,297	384,346	—	—	—	—	—	—	—	—	—	—	—	—	—
53	82,599	8,955	8,152	83,382	9,809	405,397	65.1	160.4	7.1	17.6	—	—	—	—	—	—	—	—	—
54	79,812	8,733	7,992	80,513	9,457	390,826	—	—	—	—	—	—	—	—	—	—	—	—	—
55	79,131	8,664	7,911	80,105	9,317	393,282	11.6	29.5	8.9	22.7	—	—	—	—	—	—	—	—	—
56	72,280	8,373	7,561	72,897	9,197	388,346	—	—	—	—	—	—	—	—	—	—	—	—	—
57	75,483	8,573	7,751	76,407	9,397	398,346	16.4	42.2	11.3	29.1	—	—	—	—	—	—	—	—	—
58	76,469	8,550	7,870	77,685	9,537	398,827	—	—	—	—	—	—	—	—	—	—	—	—	—
59	82,599	8,922	8,201	83,228	9,483	398,020	—	—	—	—	—	—	—	—	—	—	—	—	—
60	79,845	8,119	7,530	80,455	9,317	393,282	8.6	21.9	15.0	38.1	—	—	—	—	—	—	—	—	—
61	79,845	8,119	7,530	80,455	9,317	393,282	12.6	32.3	5.8	14.8	—	—	—	—	—	—	—	—	—
62	80,105	8,346	7,646	80,785	9,537	398,827	16.8	37.8	4.8	12.2	—	—	—	—	—	—	—	—	—
63	79,812	8,618	7,938	80,512	9,317	393,282	25.6	64.2	0.0	0.0	—	—	—	—	—	—	—	—	—
64	82,599	8,938	8,051	83,386	9,214	398,805	—	—	—	—	—	—	—	—	—	—	—	—	—
65	75,716	8,097	7,486	76,329	9,214	398,805	10.6	27.9	0.0	0.0	—	—	—	—	—	—	—	—	—
66	81,909	8,822	8,142	82,589	9,336	385,848	—	—	—	—	—	—	—	—	—	—	—	—	—
67	71,586	7,897	7,348	72,135	9,317	393,282	7.9	20.2	9.9	25.2	—	—	—	—	—	—	—	—	—
68	85,352	7,983	7,439	85,896	9,517	393,282	—	—	—	—	—	—	—	—	—	—	—	—	—
69	86,729	8,437	7,779	87,387	9,752	403,006	—	—	—	—	—	—	—	—	—	—	—	—	—
70	81,918	8,927	8,312	82,533	9,809	405,397	5.6	13.8	11.9	29.6	—	—	—	—	—	—	—	—	—
71	86,729	9,525	8,852	87,402	10,216	422,196	—	—	—	—	—	—	—	—	—	—	—	—	—
72	85,352	8,845	8,210	85,987	9,336	385,848	—	—	—	—	—	—	—	—	—	—	—	—	—
73	81,873	8,004	8,323	82,554	9,517	393,282	—	—	—	—	—	—	—	—	—	—	—	—	—
74	81,873	8,890	8,437	82,828	9,809	405,397	50.2	121.8	7.5	18.6	—	—	—	—	—	—	—	—	—
Column										Average									
Total										Total									
Feed (kg/hr)										80,505									
Steam (kg/hr)										8,651									
Overhead (kg/hr)										7,991									
Bottom (kg/hr)										81,282									
Total (kg/hr)										9,525									
Ammonia (kg/hr)										15.6									
Methanol (kg/hr)										19.1									
Methanol (ppm)										55.1									
Methanol (ppm)										55.1									

Excluded from overall averages: (—) Sample not taken and/or no data available.

TABLE 23. PRODUCTION UNIT AVERAGE PROCESS CONDITIONS

Steam Stripper	Flow (kg/hr)
Feed measured	80,500
Steam measured	8,680
Subtotal	89,180
Overhead measured	7,980
Bottoms by difference	81,200

Components Present in the Furnace Stack Exhaust

The three components of interest in the furnace exhaust stack are ammonia, methanol and nitrogen oxides. Potential sources of these components are listed in Table 24 and discussed below.

TABLE 24. SOURCE OF CONTAMINANTS IN FURNACE EXHAUST STACKS

	Ammonia	Methanol	NOx
Natural gas to fire box	Yes	No	Yes
Combustion air to fire box	No	No	Yes
Stripper overhead	Yes	Yes	No
Purge gas from synthesis loop	Yes	No	No

Natural Gas to Fire Box--

A component analysis of the natural gas used for fire box combustion revealed that it contained traces of nitrogen. Combustion of this nitrogen would be a source of nitrous oxides.

Total Fuel to Furnace Fire Box--

In addition to the natural gas used for fuel, the purge gas from the synthesis loop of the ammonia plant is burned in the fire box. It is mixed with the natural gas, and the mixture burns under the same conditions. The total component analysis of the furnace fuel gas is given in Table 25.

TABLE 25. TOTAL COMPONENT ANALYSIS OF THE FURNACE FUEL GAS

Component	Total Furnace Fuel Components		kg/hr
	Mole %	Moles/hr	
Natural gas	77.92	2500	19,088
Hydrogen	21.33	684	620
Ammonia	0.75	24	185
	100.00	3208	19,893

Conversion of Atmospheric Nitrogen and Ammonia to Nitrogen Oxides in the Furnace--

At the fire box temperatures in the reformer furnace, the conversion of atmospheric nitrogen in the intake air to nitrogen oxides is negligible. Several tests on a reformer furnace operating only on natural gas corroborate this statement. These measurements indicated that the NO_x in the exhaust gases from reformer furnaces was around 35 ppm. Since the conversion of the nitrogen in the combustion air to nitrogen oxides is minimal, the source of the nitrogen oxides in the furnace stack must be the purge gases. The furnace outlet was analyzed for NO_x, ammonia, and methanol. The data for each of these runs are summarized in Table 26. A total of 8 runs were made on the furnace exhaust gases prior to the stripper overhead injection. Previously reported values on similar plants have found NO_x concentrations ranging from 255 to 520 ppm.

TABLE 26. STACK GAS ANALYSIS PRIOR TO STRIPPER OVERHEAD INJECTION

Run Number	Ammonia (ppm)	Methanol (ppm)	NO _x (ppm)
1	0	0	156
2	0	0	233
3	0	0	163
4	0	0	244
5	0	0	160
6	0	0	115
7	0	0	148
8	0	0	157
Average	0	0	172

Stripper Overhead Theoretical Conversion to NO_x--

The data shown in Tables 21 and 22 are the average values of all the data presented in Tables 19 and 20 for the amounts and concentrations of ammonia and methanol in the stripper overhead. If all the ammonia were oxidized to NO_x in the furnace stack, the quantities indicated in Table 27 would be expected.

TABLE 27. THEORETICAL CONVERSION OF AMMONIA IN STRIPPER OVERHEAD TO NO_x

	Ammonia in Overhead		NO _x in Stack	
	mg/l	kg/hr	ppm	kg/hr
Overhead	4750	37.9	260.7	102.6
Furnace Outlet	--	--	172	67.7
Total			432.7	170.3

Conversion of Ammonia in Stripper Overhead to NOx--

Previously, the thermodynamics of degradation of ammonia and methanol were examined as a function of temperature. Based on those calculations, it was predicted that 99 percent of the methanol and 90 percent of the ammonia would decompose at the operating stack temperature of approximately 221°C. Table 28 summarizes the average of all stack analyses made to determine the individual components of ammonia, methanol, and NOx. This actual stack gas analysis shows that the ammonia and methanol from the stripper overhead have been reduced by 59.3 and 74.7 percent, respectively. This amount of degradation for those two products was somewhat less than that projected from theory. The partial pressure effects of the other components could account for this difference.

TABLE 28. AVERAGE STACK EMISSION VALUES WITH STRIPPER OVERHEAD INJECTION

	Total Stack Gases	
	ppm	kg/hr
Ammonia	39.3	15.5
Methanol	13.4	5.3
NOx	242.0	95.3

According to the Gibb's free energy calculations (Fig. 17), the decomposition of ammonia (NH_3) to nitrogen dioxide (NO_2) in the furnace stack in the presence of oxygen (O_2) is highly probable. If 100% of the ammonia (37.9 kg/hr of NH_3) out of the steam stripper overhead were converted to nitrogen dioxide in the primary reformer furnace stack by the following equation



then the 37.9 kg/hr of ammonia would be converted into 102.6 kg/hr (260.7 ppm) of nitrogen dioxide. However, 15.5 kg/hr of ammonia was detected in the primary reformer stack discharge outlet, indicating a reduction of 22.5 kg/hr and/or a decomposition of 59.2% of ammonia. Also found in the primary furnace stack discharge point was 5.3 kg/hr of methanol, indicating a reduction of 15.6 kg/hr and/or a decomposition of some 74.7% of the methanol into carbon dioxide and water. However, an increase from 67.6 kg/hr (172 ppm) to 95.3 kg/hr (242 ppm) of nitrogen oxide was observed in the primary furnace stack discharge point. This increase of 27.7 kg/hr (70 ppm) and/or 40.9% of nitrogen oxide can be related to the observed reduction of ammonia. For example, if the 22.5 kg/hr decomposition of ammonia were converted into nitrogen dioxide, this would represent an increase of 60.7 kg/hr of NO_2 . Since only a 27.7 kg/hr increase of NO_2 was observed, it is assumed that some of the ammonia decomposed into N_2 and H_2 .

SECTION 10

ECONOMIC COMPARISONS OF SELECTED TREATMENT SCHEMES FOR REMOVAL OF AMMONIA FROM PROCESS CONDENSATE

INTRODUCTION

The installation of any process equipment must be justified economically and environmentally. The economic reasons for installation of capital equipment are usually dictated by corporate policy. The cost of additional equipment to recover traces of residual intermediates or product can be analyzed against actual value in making any economic justification for this recovery.

Government regulations and popular demand for environmental improvements necessitate the recovery of process wastewater streams through operational changes and capital additions. Certain criteria should be evaluated to ensure that the removal of these contaminants from process wastewater streams does not cause undue economic hardship on the operations or result in an unacceptable price increase.

Cost comparisons were made for selected process schemes to reduce the ammonia and methanol in the process condensate. These process schemes were as follows:

- Atmospheric steam stripping of process condensate with vapor injection into furnace stack
- Reinjection steam stripper with injection of the condensed overhead into the primary furnace inlet.
- Absorption of ammonia on vanadium pentoxide catalysts to produce aqueous ammonia (28%) and/or anhydrous ammonia by-product upon regeneration of the catalyst.
- Addition of phosphates and potassium magnesium sulfate to the process condensate stream to produce a marketable by-product of magnesium ammonium phosphate fertilizer.

The economic evaluation of these processes was based on capital cost, raw materials, and operating cost. The amount of land usage for the various processes was not taken into account in the economic evaluation. In cases where by-products were formed, a product credit was given to the process and deducted from the annual cost of production. In all process cases, the following conditions were utilized in the economic evaluations:

- Straight-line, 10-year depreciation.
- Eight percent interest rate, averaged over the 10-year period.
- Approximately 331 days/year operation.
- Approximately 8,000 hr/yr operation.
- 760 l/min process condensate stream with 1000 ppm NH_3 .

PROCESS CHARACTERIZATION SCHEMES FOR ECONOMIC EVALUATION

Atmospheric Steam Stripping

Atmospheric steam stripping is a process that utilizes live steam as the driving force to strip out the ammonia in the condensate effluent via a packed column. In this case, the overheads are vented via the furnace stack of the primary reformer prior to atmospheric discharge. There are several advantages of atmospheric steam stripping via the furnace stack: it is the least expensive of all processes to operate; it is the simplest process scheme and requires least supervision; it requires only a small amount of process land area. However, with atmospheric steam stripping, there is a possibility of air pollution by NO_x .

Figure 21 shows the process scheme from which the economic evaluation was made.

Equipment Cost Estimate

<u>Equipment Cost</u>	
1. Feed storage tank	\$12,000
2. Stripping column (packed)	28,000
3. Feed preheater - 99 m ² @ \$376/m ²	35,000
4. Bottoms - 99 m ² @ \$376/m ²	35,000
5. Pumps (feed, bottoms, storage)	10,000
6. Assorted piping	10,000
Total	\$130,000
Total installed cost	\$350,000

Operating Cost for Steam Stripper--

The items which make up the operational cost of such a facility are listed below. The basis of utility cost was set forth in the design criteria.

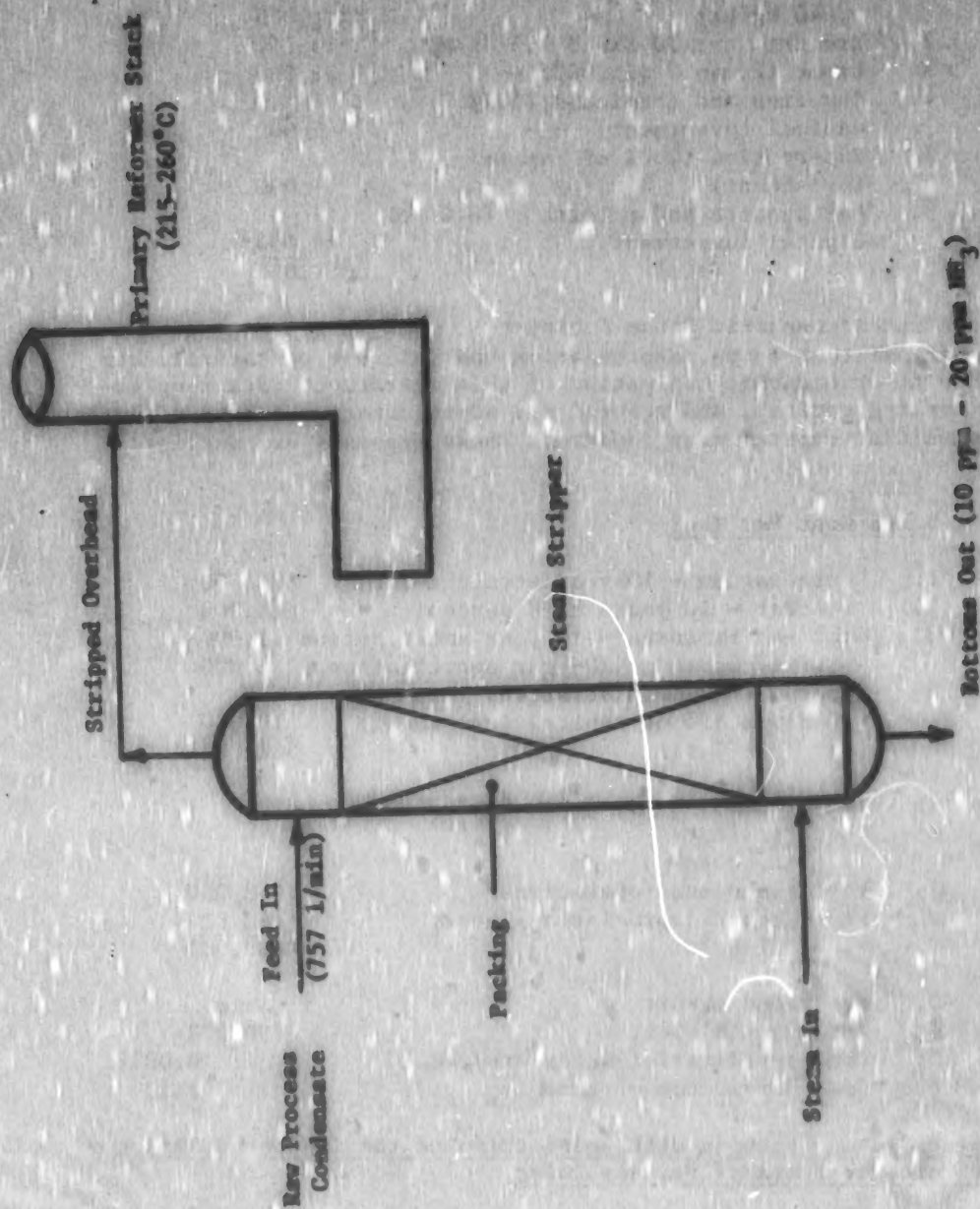


Figure 21. Atmospheric steam stripper discharge via primary reformer stack.

Operating Cost Per Year

1. Steam Consumption (\$6.61/1000 kg @ 5,440 kg/hr)	\$288,000
2. Electricity (50 KWH @ 2.5¢/KWH)	10,000
3. Labor (2 men @ \$15,000/man)	30,000
4. Supplies and chemicals (1.5% capital investment)	5,000
5. Supervision (2.0% of capital investment)	7,000
6. Maintenance and materials (8.0% of capital investment)	28,000
Total	\$368,000

Fixed Cost for Atmospheric Steam Stripper—

Two significant costs, depreciation and interest on capital, are applicable to an economic evaluation of this operation. Start-up expenses, working capital, and general and administrative corporate expenses increase initial capital requirements. These expenses are outlined below.

Fixed Cost Per Year

1. Depreciation - 10-year straight-line	\$35,000
2. Interest - 10 years at 8 percent	15,000
3. Start-up expenses - 10-year amortization	1,000
4. Working capital - 10-year amortization	1,000
5. General and administrative, insurance and taxes (3% of capital investment)	10,000
Total	\$62,000

Cost-Benefit Value of Atmospheric Steam Stripping— Cost Per Year

1. Variable costs (operations)	\$368,000
2. Fixed cost (depreciation, etc.)	62,000
Total	\$430,000
3. Recovered credit	None
4. Total annual Cost	\$430,000
5. Cost per liter of water treated	\$ 0.0012
6. Cost per m. ton of ammonia	\$ 1.50

Atmospheric Steam Stripping with ReInjection of the Condensed Stripper Overhead into the Primary Furnace Inlet

In the reinjection process, instead of being discharged to the atmosphere, the overheads of the steam stripper are condensed, pressurized, and reinjected into the primary reformer. Although there would be practically zero discharge of pollutant to the environment, there would be an increase in natural gas requirements; an increase in cooling water and cooling tower usage; and an increase in tower height, packing material, and foundation strength. Figure 22

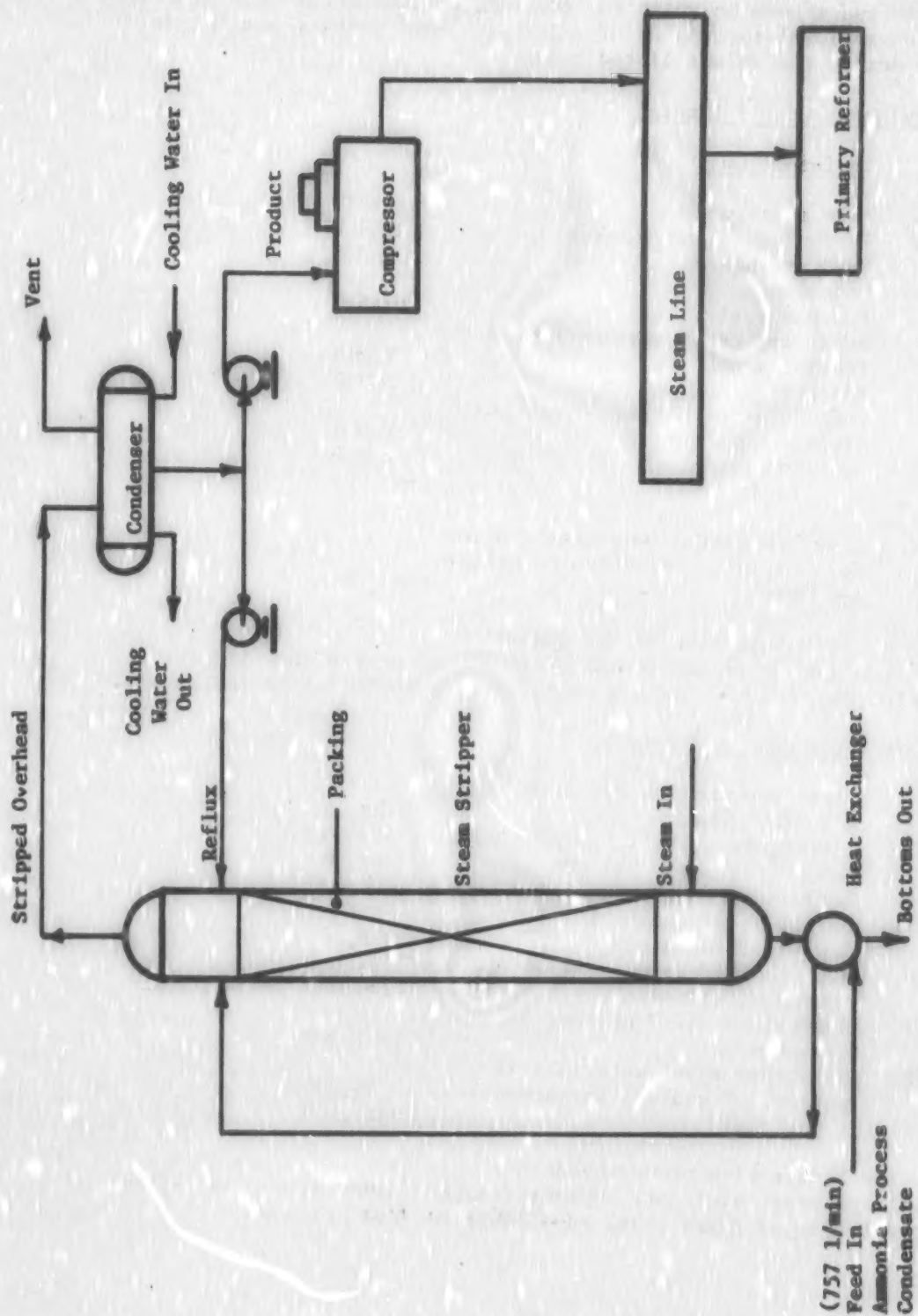


Figure 22. Reinjection of steam stripped process condensate into primary reformer via steam injection.

shows the process scheme on which the economic evaluation of this process was made. Conventional techniques of major equipment pricing and factoring were used to derive the values listed below.

Equipment Cost Estimate

Equipment Cost

1.	Feed storage tank	\$12,000
2.	Stripping column (packed)	28,000
3.	Feed pre-heater	35,000
4.	Condenser	7,000
5.	Bottoms cooler	20,000
6.	Separator drum, overheads drum (collection)	3,000
7.	Sparger	2,000
8.	Pumps (feed, bottoms, overheads, storage, sparger)	35,000
9.	Assorted piping	20,000
	Total	<u>\$162,000</u>

Total installed cost (also boiler for heating reinjection to primary reformer) \$600,000

Operating Cost for Reinjection of Overheads--

Items contributing to the operational cost of such a facility are listed below. The basis of utility cost were set forth in the design criteria.

Operating Cost Per Year

1.	Steam consumption (\$6.61/1000 kg @ 7,260 kg/hr)	\$384,000
2.	Electricity (150 KWH @ 2.5¢/KWH)	30,000
3.	Labor (4.5 men @ \$15,000/man)	67,500
4.	Reflux overheads and cooling water	20,000
5.	Supplies and chemicals (1.5% capital investment)	9,000
6.	Fuel cost (furnace - \$49.44/1000 m ³ 3 percent increase)	244,000
7.	Supervision (2.0 percent of capital investment)	12,000
8.	Maintenance and materials (8.0 percent of capital investment)	48,000
	Total	<u>\$814,500</u>

Fixed Cost for Reinjection of Overheads--

As with the steam stripper, depreciation and interest on the capital required are the major fixed costs applicable to this process.

Fixed Costs Per Year

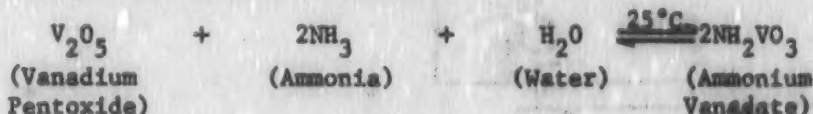
1.	Depreciation - 10-year straight line	\$ 60,000
2.	Interest - 10 years @ 8 percent	26,400
3.	Start-up expenses	15,000
4.	Working capital	15,000
5.	General and administrative, insurance and taxes (3% of capital investment)	18,000
	Total	\$134,400

Cost-Benefit Value of Reinjection of Overheads-- Cost Per Year

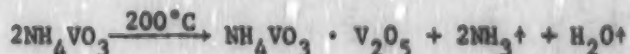
1.	Variable costs (operations)	\$814,500
2.	Fixed cost (depreciation, etc.)	134,400
	Total	\$948,900
3.	Recovered credit	None
4.	Total annual cost	\$948,900
5.	Cost per liter of water treated	\$ 0.0026
6.	Cost per m. ton of ammonia	\$ 3.20

Vanadium Pentoxide Catalyst Absorption

In this process, air stripping of the process condensate stream is the first step. The overhead vapor (NH_3 , H_2O vapor, and air) is passed through a bed of vanadium pentoxide catalyst, resulting in the chemical reaction illustrated by the following equation.



After absorption of ammonia as ammonium vanadate, the catalyst can be regenerated by heating to 450°C or steam regeneration at 200°C . However, at the lower temperature, stable intermediates are formed. According to the literature(11), the regeneration of 200°C indicated about two-thirds of the ammonia was evolved. Under these conditions, the reaction proceeds as follows:



The evolved ammonia can be condensed, with enough water subsequently added to produce aqueous ammonia of commercial strength (28% NH_3); or the gaseous stream can be dried over caustic or soda lime, and the resulting anhydrous ammonia stored as a liquid under pressure.

The process shown in Figure 23 utilizes a triple sequence of fixed catalyst beds for the ammonia absorption. The air stripped ammonia goes into the bottom, is absorbed to the V_2O_5 catalyst, and exits the top of the absorbers (A, B and C). It can either be vented to the air or recycled back

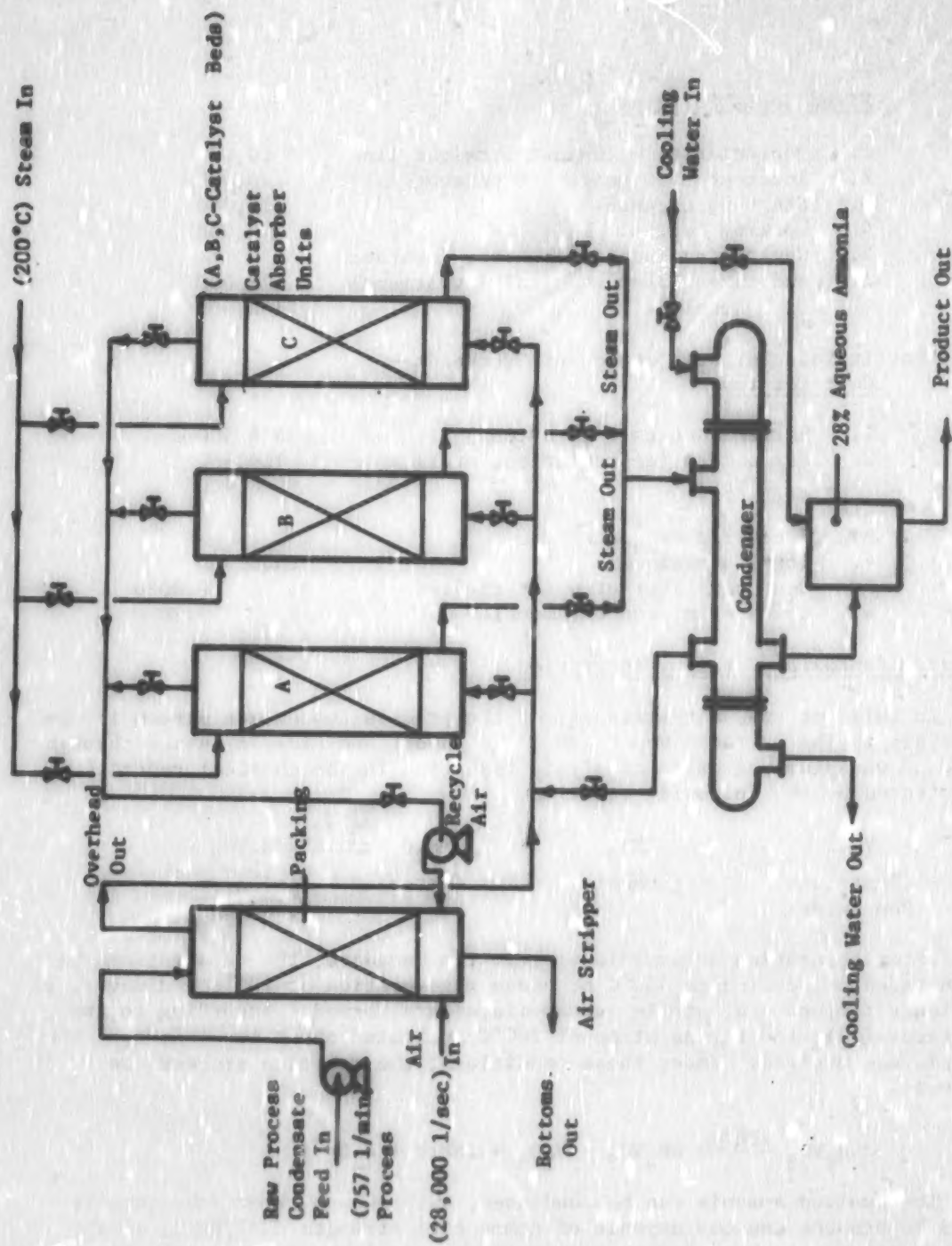


Figure 23. Vanadium pentoxide catalyst absorption.

into the stripper. This process was designed on a three-day cycle. While absorber A is being used for the absorption, absorber B is being regenerated and cooled to room temperature for reuse after absorber A has completed its cycle. The air stream from the unit being used as the absorber could be used to cool down the unit after regeneration and thus speed up the cycle.

A fixed bed (semibatch) instead of a continuous absorber, was used in the economic evaluation(12,13). This process would require a smaller capital investment, but possibly would suffer a greater loss of catalyst. In the vanadium pentoxide absorber system, there is practically zero discharge of pollutant to the environment. Further, the system reclaims a product which was once discarded to the environment. It is a relatively simple process, and the absorbency power of catalysts upon regeneration is very good. Disadvantages of the vanadium pentoxide absorber are: (1) the cost of catalysts is relatively high (\$6.75/kg); (2) regeneration losses could occur; (3) power requirement for air stripper is high (the process requires approximately 2.2 m³ of air per liter of condensate stripper); (3) only two-thirds of the NH₃ in catalysts bed is removed per regeneration when 200°C steam is used, and (4) no removal of methanol is indicated.

Capital Cost for Vanadium Pentoxide Absorber--

Basis:

1. 331 days/year and/or 8,000 hours/year.
2. Straight-line 10-year depreciation.
3. Interest on capital investment at 8 percent with a 10-year payout.
4. 760 l/min ammonia process condensate treatment (1000 ppm ammonia).
5. Initial charge of catalysts included in capital investment (\$150,000).
6. Assume 1% loss of catalyst per regeneration.
7. Using air stripping prior to catalysts absorbers (2.2 m³ air/liter of treated water).

Equipment Cost Estimate

Equipment Cost

1.	Feed storage tank	\$12,000
2.	Stripping column (packed)	28,000
3.	Initial catalysts charge	150,000
4.	Absorbing column (3)	75,000
5.	Condenser (11.3 m ² @ \$1236/m ²)	14,000
6.	Product holding and storage tank	20,000
7.	Pumps	25,000
8.	Fans (2.2 m ³ air/liter of treated water)	16,000
9.	Assorted piping	60,000
	Total	\$400,000
	Total installed cost	\$1,600,000

Operating Cost for Vanadium Pentoxide Absorber--

These calculations followed the pattern used in assessment of the operating cost of the steam stripper.

Operating Cost Per Year

1.	Air stripper power (2047 KWH @ 2.5¢/KWH)	\$409,000
2.	Steam cooling H ₂ O (regeneration)	20,000
3.	Electricity (150 KWH @ 2.5¢/KWH)	30,000
4.	Labor (4.5 men @ \$15,000/man)	67,500
5.	Supplies and chemicals (1.5% of capital investment)	24,500
6.	Supervision (2.0% of capital investment)	32,000
7.	Maintenance and materials (8 percent of capital investment)	128,000
8.	V ₂ O ₅ catalyst replacement (1 percent loss/regeneration)	180,000
	Total	\$890,500

Fixed Cost for Vanadium Pentoxide Absorber--

As in the previous evaluations, the two fixed costs of interest are depreciation and interest on the capital required. The actual capital required would have to be larger than needed for equipment installation as a result of start-up expenses, working capital, and general and administrative corporate business expenses. These figures are outlined below.

Fixed Costs Per Year

1.	Depreciation - 10-year straight line	\$160,000
2.	Interest - 10 years @ 8 percent	70,400
3.	Start-up expenses	35,000
4.	Working capital	35,000
5.	General and administrative, insurance and taxes (3 percent of capital investment)	48,000
	Total	\$348,400

Recovered Product Credit for Vanadium Pentoxide Absorber--

The average ammonia concentration of the process condensate effluent taken was 1000 ppm. At a 757 l/min process condensate wastewater stream, approximately 907 kg of ammonia per day is recovered.

Aqueous Ammonia Recovered Product Credit--

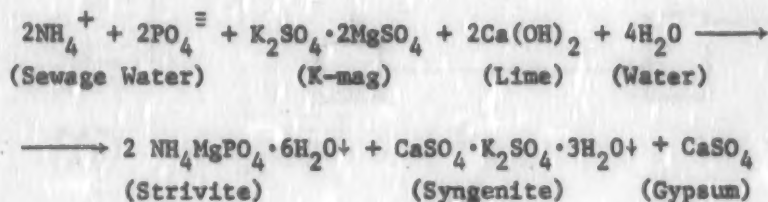
1.	Flow	\$45,360 kg/hr
2.	NH ₃	45.4 kg/hr
3.	Aqueous NH ₃ (28 percent)	3000,283 kg/yr
4.	Aqueous NH ₃ (28 percent) @ 20.39¢/kg	\$16,000 per year

**Cost-Benefit Value for Vanadium Pentoxide Absorber—
Cost Per Year**

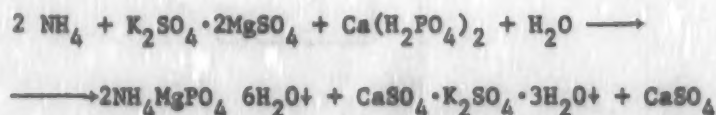
1. Variable costs (operations)	\$890,500
2. Fixed cost (depreciation, etc.)	348,400
Total	\$1,238,900
3. Recovered credit	61,000
4. Total annual cost	\$1,177,900
5. Cost per liter of water treated	\$ 0.003
6. Cost per m. ton of ammonia	\$ 3.94

Conversion of NH_3 to Magnesium Ammonia Phosphate

The conversion of NH_3 to magnesium ammonia phosphate utilizes several chemicals. The following equation shows the chemical reaction which occurs:



This process has been focused on recovery of ammonia through treatment of municipal sewage and should be applicable to recovery of ammonia from the process condensate.



In applying the above equation to the ammonia process, ammonia water and $\text{Ca}(\text{H}_2\text{PO}_4)_2$ would replace the sewage water and $\text{Ca}(\text{OH})_2$, respectively. This modified equation was used in the evaluation of this process. Figure 24 shows the process scheme for which the economic evaluation was made. Advantages are that there is practically zero discharge of pollutants to the environment and a product which was once discarded to the environment could be reclaimed. However, a large capital investment is required; a by-product has to be marketed, a large land area and product storage facilities are needed.

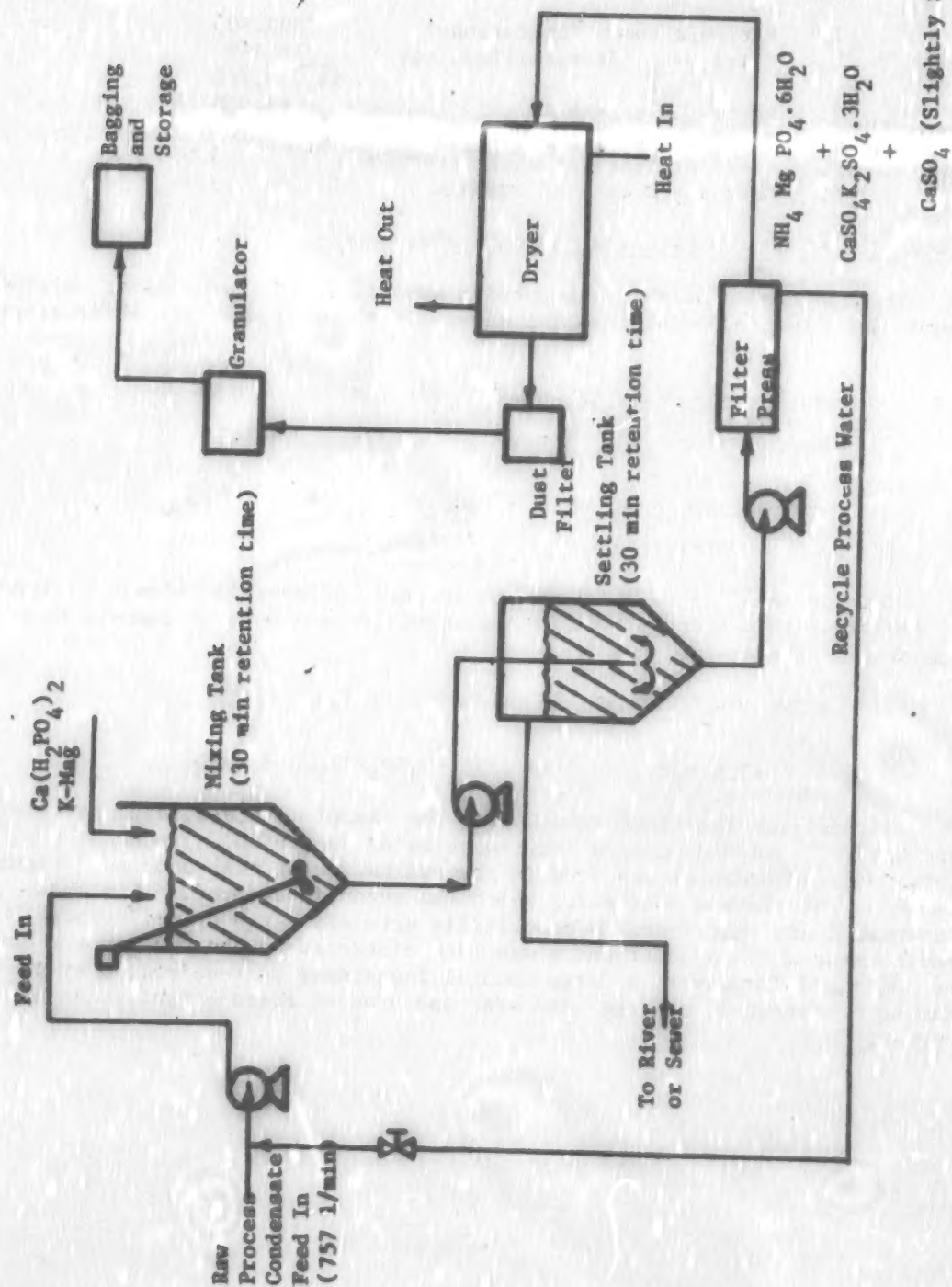


Figure 24. Magnesium ammonium phosphate process.

The procedures described above were used to make the following calculations.

Capital Cost for Magnesium Ammonia Phosphate--

Equipment Cost Estimate

Equipment Cost

1.	Feed storage tank	\$12,000
2.	Mixing tank	15,000
3.	Settling tank	7,000
4.	Filter press	50,000
5.	Dryer	20,000
6.	Granulator	60,000
7.	Pumps	40,000
8.	Assorted piping	60,000
9.	Stirrers and mixers	40,000
10.	Bagging and storage	100,000
	Total	<u>\$404,000</u>
	Total installed cost	\$1,500,000

Operating Cost for Ammonium Phosphate--

Operating Cost Per Year

1.	Raw materials	
2.	K-mag	\$235,500
3.	Ca (H ₂ PO ₄) ₂	290,300
4.	Fuel for drying and electrical	535,000
5.	Bagging by-product (\$11/m. ton)	57,600
6.	Labor (6.0 men @ \$15,000/man)	90,000
7.	Supplies and chemicals (1.5% of capital investment)	22,500
8.	Supervision (2 percent of capital investment)	30,000
9.	Maintenance and materials (8 percent of capital investment)	<u>120,000</u>
	Total	<u>\$1,380,900</u>

Fixed Cost for Magnesium Ammonium Phosphate--

Fixed Costs Per Year

1.	Depreciation - 10 year straight line	\$150,000
2.	Interest - 10 years @ 8 percent	70,400
3.	Start-up expenses	30,000
4.	Working capital	30,000
5.	General and administrative, insurance and taxes (3 percent of capital investment)	<u>45,000</u>
	Total	<u>\$325,400</u>

Recovered Product Credit for Magnesium Ammonium Phosphate--

The average ammonia concentration of the process condensate effluent was 1000 ppm. For a 757 l/min process condensate wastewater stream, approximately 907 kg of ammonia per day is recovered.

Magnesium Ammonium Phosphate Recovered--

1. Flow	\$45,360 kg/hr
2. NH_3	45.4 kg/hr
3. Phosphate (CaH_2PO_4) ₂	449 kg/hr
4. Magnesium (K-mag)	725 kg/hr
5. Magnesium ammonium phosphate	5,226,000 kg per year
6. Magnesium ammonium phosphate at 5.5¢/kg	\$288,000 per year

Cost-Benefit Value for Magnesium Ammonium Phosphate-- Cost Per Year

1. Variable costs (operations)	\$1,380,900
2. Fixed cost (depreciation, etc.)	325,400
Total	\$1,706,300
3. Recovered credit	288,000
4. Total annual cost	\$1,418,300
5. Cost per liter of water treated	\$ 0.004
6. Cost per m. ton of ammonia	\$ 4.41

SUMMARY OF ECONOMIC EVALUATION

A summary of the economic evaluations for each process is presented in Tables 29 and 30. As indicated in Table 29, the atmospheric steam stripper is the least expensive to operate; the magnesium ammonium phosphate process is the most expensive. Using the atmospheric steam stripper as the basis, Table 30 shows the cost ratio of each process and also the cost per liter to treat process condensate prior to river discharge.

TABLE 29. ECONOMIC EVALUATION OF VARIOUS PROCESSES

Process	Subtotal Cost/Yr	Product Credit/Yr	Total Cost/yr
Atmospheric Steam Stripper Reinjection into Primary	\$ 449,150	None	\$ 449,150
Reformer	\$ 948,000	None	\$ 948,000
Vanadium Pentoxide Phosphate	\$1,706,300	\$ 61,000	\$1,177,900
Magnesium Ammonium Phosphate	\$1,706,300	\$288,000	\$1,418,300

TABLE 30. PROCESS COST RATIOS AND COST PER LITER OF INFLUENT

Process	Cost Ratio	Liters/Yr Processed	Cost/Liter
Atmospheric Steam Stripper Reinjection into Primary Reformer	1	363,360,000	\$0.0012
Vanadium Pentoxide Catalysts	2.11	363,360,000	\$0.0026
Magnesium Ammonium Phosphate	2.76	363,360,000	\$0.003
	3.79	363,360,000	\$0.004

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